DISTRIBUTION OF AQUATIC ANIMALS RELATIVE TO NATURALLY ACIDIC WATERS IN THE SIERRA NEVADA

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Supporting Study

GEOLOGICAL CONTROLS ON NATURAL ACIDIFICATION OF ALPINE LAKES IN THE EASTERN SIERRA NEVADA

Contract No. A132-192

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ABSTRACT

We surveyed chemical conditions and the presence/absence of vertebrate populations in 104 lakes in the Bench Lake/Mt. Pinchot area of Kings Canyon National Park in early summer of 1992. These lakes ranged in pH from 5.0 to 9.3, and included 10 lakes with pH's < 6.0 (defined herein as acidic lakes). On the basis of this initial survey, 33 lakes were chosen for detailed analyses of their chemical and biological characteristics, including 8 acidic lakes.

Lake water composition data for 33 lakes in the detailed survey indicate that these lakes are all unusual in comparison to typical Sierra Nevada lakes sampled in previous surveys. Unlike typical Ca-Na-HCO_3-dominated Sierra lakes, SO_4 concentrations are high enough to classify 19 of these lakes with SO_4 as the dominant anion. Furthermore, 25% of the lakes surveyed had pH values less than 6 and essentially 0 ANC. The source of the acidity and SO_4 is sulfuric acid produced by the oxidation of pyrite found in metamorphic and granitic rocks in the area. Neutralization of acidity occurs downstream mostly by dilution with circumneutral water of lower ionic strength. This provides a chemical gradient along which various species of aquatic life may distribute themselves. This area appears to provide a good model for long-term acidification effects on aquatic ecosystems.

The faunal surveys revealed that mountain yellow-legged frog tadpoles (Rana muscosa), limnephilid caddis larvae (Hesperophylax), and large microcrustaceans (Daphnia, Diaptomus) were rare or absent in lakes having pH's < 6, but were commonly collected from lakes with pH's ≥ 6. Trout belonging to four species were collected from or observed in a small proportion of the study lakes, and trout distributions appeared to be related to historical stocking patterns. The distribution of trout appeared to have large effects on the distributions and abundances of amphibian and invertebrate taxa, with large, mobile, and conspicuous taxa being rare or absent in trout lakes, but relatively common in lakes lacking trout. The results suggest that increased acidification of High Sierra lakes will result in the elimination of larval amphibians, large microcrustaceans, and a few macroinvertebrates from lakes, and a decline in microcrustacean species richness. Currently, however, the most profound human impacts on aquatic communities in the High Sierra appear to be related to historical and on-going stocking of exotic fish species into High Sierra waters.

DISCLAIMER

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SUMMARY AND CONCLUSIONS

Acidification of lakes and streams by atmospheric deposition can seriously affect the aquatic biota. In the Sierra Nevada of California, acidic deposition has been reported in the Tahoe basin, and on both the eastern and western slopes. The lakes and streams of the Sierra Nevada are among the most weakly buffered in the world, and are thus susceptible to acidification by atmospheric deposition. Owing to a series of studies supported by the California Air Resources Board (CARB), our knowledge of biotic responses to acidification in the Sierra Nevada has increased substantially. These investigations have included detailed examinations of the hydrochemistry and aquatic ecology of High Sierra waters, including surveys of relationships between hydrochemistry and the aquatic biota; time series analyses on chemical and biological parameters; and field and/or laboratory experiments on the effects of different acid levels on planktonic and benthic assemblages, fish, and amphibians. All experiments conducted on the responses of aquatic animals from Sierran waters to acid input have used lake bags, streamside channels, or laboratory systems. A limitation of these studies is that the degree to which they are applicable to whole ecosystems over long time periods is not clear.

The recent discovery of a series of naturally-acidic lakes in the High Sierra has provided scientists with a "natural experiment" for assessing the long-term effects of acidity on the biota of lakes. The studies described in this report include comparisons of chemical conditions, and the characteristics of zooplankton, macroinvertebrate, fish, and amphibian assemblages, in acidic and nearby circumneutral lakes occupying a small area in the Sierra Nevada. The results of these surveys allow us to check for congruence with results of previous small-scale field and laboratory experiments, extend field observations to more acidic conditions than previously found, and provide a better basis for predicting the potential effects of increased acid inputs on High Sierra lakes.

The authors of this report and their colleagues surveyed chemical conditions and the presence/absence of vertebrate populations in 104 lakes in the Bench Lake/Mt. Pinchot area in early summer of 1992 ("Synoptic Survey"). These lakes ranged in pH from 5.0 to 9.3, and included 10 lakes with pH's < 6.0 (defined herein as acidic lakes). On the basis of this initial survey, 33 lakes were chosen for detailed analyses of their chemical and biological characteristics, including 8 acidic lakes ("Detailed Survey"). Samples of water chemistry, fish, amphibians, zooplankton, and macroinvertebrates were collected from these lakes in August and early September, 1992, and water samples were

taken from 10 of these lakes in late September, 1992, to check for seasonal variation in water quality parameters.

The specific objectives of the project were the following: (1) Describe the surface water chemistry (pH, acid neutralizing capacity [ANC], electrical conductivity [EC], major ion composition, and aluminum concentrations) in acidic and nearby non-acidic lakes of the Bench Lake/Mt. Pinchot area of the Sierra Nevada. (2) Identify potential sources of acidity for the acidic lakes in this area through an analysis of geological conditions and patterns in water quality data. (3) Determine the distributions of aquatic-breeding amphibians, fish, macroinvertebrates, and zooplankton in relationship to pH. (4) Examine the degree of congruence between the water chemistry associated with presence/absence of organisms in the field and the results of previous experimental and survey studies.

Chemical Composition of Lake Water

Lake water composition data for 33 lakes in the Bench Lake-Mt. Pinchot area of the eastern Sierra Nevada indicate that these lakes are all unusual in comparison to typical Sierra Nevada lakes sampled in previous surveys. Unlike typical Ca-Na-HCO_3-dominated Sierra lakes, SO_4 concentrations are high enough to classify 19 of these lakes with SO_4 as the dominant anion. Furthermore, 25% of the lakes surveyed had pH values less than 6 and essentially 0 ANC. The source of the SO_4 is the highly acidic oxidation products of pyrite weathering. The effect of the H_2SO_4 has been to titrate the ANC of various lakes by different amounts, presumably depending on the amount of pyrite present in each watershed. Below pH 6, increased H_2SO_4-acidity resulted in increased concentrations of Al, sum of base cations, and NO_3. Increased mineral solubilities explain the Al and base cation trends, but the reason for the NO_3 trend is not as clear. Increased Mg in more acidic lakes is an indication of increased weathering of mafic minerals, but it is ambiguous whether this is a consequence of acidification or merely an association with the presence of pyrite.

Geochemistry of Watershed Acidification

The source of acidity in the Mt. Pinchot area is sulfuric acid produced by the oxidation of pyrite found in metamorphic and granitic rocks in the area. Soils, volcanic activity, mineral springs, and acidic deposition can be ruled out as sources of acidity. The pyrite-bearing formations in the Mt. Pinchot area are highly localized and their

influence on surface waters is mediated by the hydrologic characteristics of each watershed. From a geochemical point of view, this system is analogous to acidic mine drainage.

Consistent correspondence was found between acid affected or acidic lakes and the spatial distribution of pyrite-rich outcrops. Not all lakes affected by acidity have low pH. Many of the affected lake-watersheds have sufficient neutralization capacity to maintain neutral pH although SO_4 levels are high. The composition of the acidic (pH < 6) and acid-affected (high $[SO_4]$) lakes is controlled in part by the solubility of the minerals jurbanite ($AlOHSO_4$) and amorphous aluminum hydroxide ($Al(OH)_3$ (a)). This has been verified by solution equilibrium calculations and mineralogical analyses of the white precipitate along the margins of acidified lakes and streams.

The hydrology of these lake watersheds has an important influence on the intensity of acidification found in surface waters. Watersheds with rock glaciers providing both a mechanical weathering force and water had the most intense acidity in the summer. Where water-pyrite contact was limited, acid production was lower. This situation is hypothesized to change during snow melt, when water-pyrite contact would be greater.

An important question arising from these analyses is whether this geochemical system is an appropriate model for the effects of long-term acidification of Sierra Nevada watersheds. Neutralization of acidity occurs downstream mostly by dilution with circumneutral water of lower ionic strength. This provides a chemical gradient along which various species of aquatic life may distribute themselves. The chemistry of the watershed neutralization process is not important to this model, only that the composition of the surface waters is similar to what might result from acidic deposition. As a result, this area appears to provide good model for acidification effects on aquatic ecosystems.

Faunal Assemblages in Acidic and Non-acidic Lakes

Trout were found in 18 of the 104 lakes in the Synoptic Survey, and 7 of the 33 lakes in the Detailed Survey. Species were rainbow trout (Oncorhynchus mykiss), golden trout (Oncorhynchus aguabonita), brook trout (Salvelinus fontinalis), and brown trout (Salmo trutta). The distribution of trout appeared to be explained primarily by stocking history, rather than water chemistry. Stocking records indicate that trout were generally planted in the largest, deepest, and most accessible lakes near the John Muir Trail and, in some cases, spread to other lakes through connecting streams. Only one acidic (pH < 6.0) lake has stocking records, yet trout do not occur there now; however,

suitable breeding habitat is lacking in this lake, and fish could have died of old age instead of inhospitable water chemistry.

Among amphibians the mountain yellow-legged frog (Rana muscosa) was found in many lakes (36 of 104 in Synoptic Survey and 20 of 33 in Detailed Survey), whereas the Pacific chorus frog (Pseudacris [=Hyla] regilla) was found in only a few lakes in the Synoptic Survey and none in the Detailed Survey. Tadpoles of the yellow-legged frog were restricted almost exclusively to lakes lacking fish, and exclusively to non-acidic ($pH \geq 6.0$) lakes. Adults were more tolerant of both the presence of fish and acidic conditions. The sensitivity of tadpoles to low pH appeared to be greater in the field (i.e., absence at $pH < 6.0$) in comparison to previous laboratory experiments (e.g., no adverse effects on survival at $pH \geq 4.75$ or growth at $pH \geq 5.5$).

The distributions of most macroinvertebrate taxa showed no relationship to lake acidity; however, one limnephilid caddis larva, Hesperophylax, was absent in acidic lakes. Large-bodied microcrustacean zooplankton (Daphnia spp., Diaptomus spp.) were rare or absent in acidic lakes but common in non-acidic lakes which lacked fish, but the distributions of chydorid cladocerans and common rotifers were unrelated to lake pH. These results show excellent qualitative agreement with the results of previous small-scale experimental studies; however, quantitative comparisons were hampered by high variability in the survey data.

The largest, current anthropogenic impact on high-altitude lakes in the Sierra Nevada has resulted from the introduction of exotic fish species. The results of the present study and others indicate that the introduction of fish has had profound effects on the structure of faunal assemblages in High Sierra lakes. Large and/or mobile, conspicuous taxa, including tadpoles, large-bodied microcrustacean zooplankton, baetid and siphlonurid mayflies, hemipterans (notonectids, corixids), limnephilid caddis larvae, and dytiscid beetles, were rare or absent in lakes containing fish, but were commonly collected in lakes lacking fish.

Summary of Effects of Lake Acidity and Introduced Fishes

In summary, our surveys of acidic and non-acidic lakes in the Bench Lake/Mt. Pinchot area of Kings Canyon National Park revealed that yellow-legged frog tadpoles (Rana muscosa), limnephilid caddis larvae (Hesperophylax), and large microcrustaceans (Daphnia, Diaptomus) were rare or absent in lakes having pH's < 6, but were commonly collected from lakes with pH's ≥ 6. These results have augmented previous survey data to include more acidic conditions. Trout belonging to four species were

collected from or observed in a small proportion of the study lakes, and trout distributions appeared to be related to historical stocking patterns. The distribution of trout appeared to have large effects on the distributions and abundances of amphibian and invertebrate taxa, with large, mobile, and conspicuous taxa being rare or absent in trout lakes, but relatively common in lakes lacking trout. The results suggest that increased acidification of High Sierra lakes will result in the elimination of larval amphibians, large microcrustaceans, and a few macroinvertebrates from lakes, and a decline in microcrustacean species richness. At the current time, however, the most profound human impacts on aquatic communities in the High Sierra appear to be related to historical and on-going stocking of exotic fish species into High Sierra waters.

RECOMMENDATIONS

1. A long-term monitoring program of water chemistry and faunal assemblages is needed to determine if, and when, natural systems begin to respond to anthropogenic acidification. Such a program is needed because short-term surveys may not capture critical conditions. Moreover, quantitative results from experimental studies may be difficult to apply to regional assessments of acidification threats to aquatic resources because of the high variability in abundance data across lakes (e.g., zooplankton) and temporal variability within and between years. Furthermore, some organisms such as amphibians appear to show greater sensitivity to water chemical conditions in the field than has been demonstrated in the laboratory. Nevertheless, the combination of quantitative experimental studies and long-term monitoring could provide the most powerful approach for detecting effects of anthropogenic acidic deposition on aquatic organisms.

2. Further research should be conducted to understand the effects of water chemistry on amphibian distribution in the Sierra Nevada, and potential causes for amphibian population declines in the region. The apparent difference in sensitivity to low pH between the field and laboratory for mountain yellow-legged frog tadpoles may have resulted for any of a number of possible reasons. For example, water chemical parameters other than pH differed between the field and laboratory conditions, laboratory studies were limited to embryos and young tadpoles at a single temperature, and field sampling may not have captured the most detrimental chemical conditions. Moreover, amphibians of several species have shown dramatic population declines in the Sierra Nevada in recent decades, yet the causes for the declines are unclear. Atmospheric inputs have been suspected because of the widespread distribution of the declines, including acidic inputs, pesticides, artificial estrogens, and climate change due to increased atmospheric CO_2.

Chapter 1
INTRODUCTION

BACKGROUND

Acidification of lakes and streams by atmospheric deposition can seriously affect the aquatic biota (Schindler et al. 1985). Responses of freshwater animal assemblages to acidification commonly include a reduction in species diversity and biomass and a shift in dominant species (Marmorek 1984, Havens and DeCosta 1987, Ormerod et al. 1987, Hall and Ide 1987, Hopkins et al. 1989; Okland and Okland 1986). Many fish species, in particular, are susceptible to increased acid inputs, and acidification can result in the local extinction of some species (Magnuson et al. 1984).

In the Sierra Nevada of California, acidic deposition has been reported in the Tahoe basin, and on both the eastern and western slopes (Leonard et al. 1981, Dozier et al. 1987, Stohlgren and Parsons 1987, California Air Resources Board 1988). The lakes and streams of the Sierra Nevada are among the most weakly buffered in the world (Landers et al. 1987), and are thus susceptible to acidification by atmospheric deposition (Melack et al. 1987, 1989).

The biological effects of lake acidification have been studied primarily in eastern North America and Europe. Application of the results of these studies to the high-altitude lakes of the Sierra Nevada may not be appropriate because of differences in climate, hydrology, and biotic assemblages. Until recently, then, there was little information on the current and predicted effects of acidity on animal communities in High Sierra lakes. Owing to a series of studies supported by the California Air Resources Board (CARB), our knowledge of biotic responses to acidification in the Sierra Nevada has increased substantially. These investigations have included detailed examinations of the hydrochemistry and aquatic ecology of High Sierra waters, including surveys of relationships between hydrochemistry and the aquatic biota, time series analyses on chemical and biological parameters, and field experiments on the effects of different acid levels on planktonic and benthic assemblages (Melack et al. 1987, 1989; Barmuta et al. 1990; Cooper at al. 1988a, 1988b).

Of particular interest are recent CARB-sponsored projects that survey the condition of populations of vulnerable aquatic species in the Sierra Nevada, and experiments that determine the responses of these species to episodic acidification (Bradford et al. 1993; Jenkins and Kratz 1991). The goal of these studies has been to assess the current status of aquatic ecosystems in the High Sierra, and to combine survey

and descriptive approaches to predict the responses of biological resources over large regions to increased acidification. All experiments conducted on the responses of aquatic animals from Sierran waters to acid input have used lake bags, streamside channels, or laboratory aquaria (Melack et al. 1987, 1989; Cooper et al. 1988b; Hopkins et al. 1989; Barmuta et al. 1990). A limitation of these studies is that the degree to which they are applicable to whole ecosystems over long time periods is not clear.

The recent discovery of a series of naturally-acidic lakes in the High Sierra has provided scientists with a "natural experiment" for assessing the long-term effects of acidity on the biota of lakes. The studies described in this report include comparisons of chemical conditions, and the characteristics of zooplankton, macroinvertebrate, fish, and amphibian assemblages, in acidic and nearby circumneutral lakes occupying a small area in the Sierra Nevada. The results of these surveys allow us to check for congruence with results of previous small-scale field and laboratory experiments, extend field observations to more acidic conditions than previously found, and provide a better basis for predicting the potential effects of increased acid inputs on High Sierra lakes.

NATURALLY-ACIDIC LAKES AND THE DESIGN OF THIS STUDY

In the 1980's a high-elevation lake in the Sierra Nevada (Lake C-24 here; "Lake 45" in Whiting et al. [1989]) was discovered which had a pH of 5.2 (Whiting et al. 1989), much lower than the lowest summer pH reported for other lakes in the Sierra Nevada (5.7) (Melack et al. 1985, Landers et al. 1987, Melack et al. 1989). The pH of this lake was also lower than all but one of the lakes surveyed in the western U.S. by the EPA Western Lake Survey (Landers et al. 1987, Whiting et al. 1989). In subsequent surveys in the summer of 1991, two research teams funded by CARB recorded a pH of 4.7 and extremely high sulfate levels for Lake C-24 (Jenkins et al., unpublished; Bradford et al., unpublished). In addition, these two survey teams discovered that the area around Lake C-24, the Bench Lake/Mt. Pinchot area in Kings Canyon National Park, contained a mixture of acidic and non-acidic lakes.

With funding from CARB, the authors of this report and their colleagues surveyed chemical conditions and the presence/absence of vertebrate populations in 104 lakes in the Bench Lake/Mt. Pinchot area in early summer of 1992 ("Synoptic Survey"; Fig. 1.1). These lakes ranged in pH from 5.0 to 9.3, and included 10 lakes with pH's < 6.0. On the basis of this initial survey, 33 lakes were chosen for detailed analyses of their chemical and biological characteristics, including 8 lakes with pH's < 6.0 ("Detailed Survey"). Samples of water chemistry, fish, amphibians, zooplankton, and

macroinvertebrates were collected from these lakes in August and early September, 1992, and water samples were taken from 10 of these lakes in late September, 1992, to check for seasonal variation in water quality parameters.

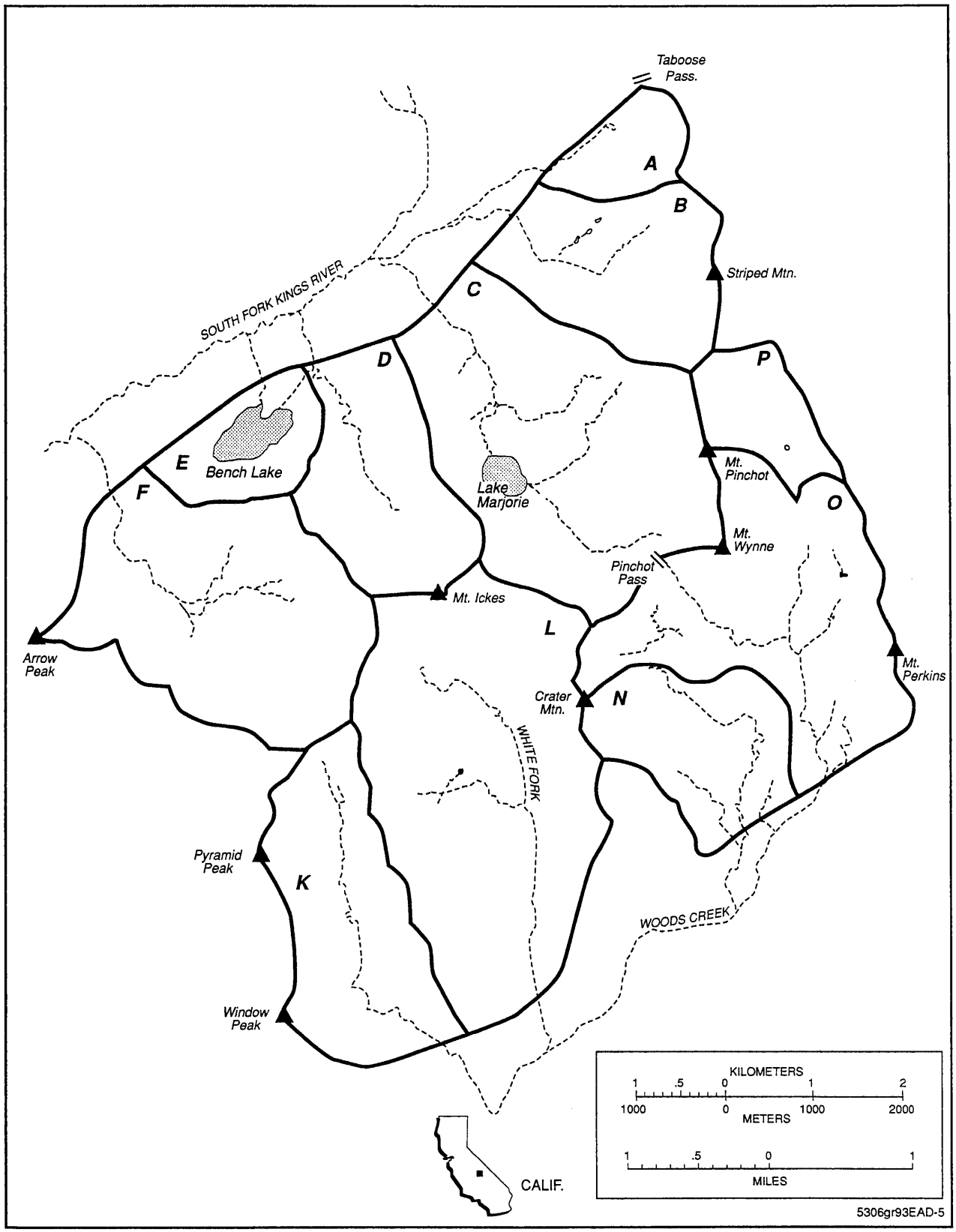
STUDY AREA AND LAKES SELECTED FOR STUDY

The study area was delineated to encompass the acidic and circumneutral lakes previously observed, and to include much of the geological formations associated with these water bodies (Moore 1962). The study area is approximately 50 square kilometers in area and is located in the Bench Lake/Mt. Pinchot area of Kings Canyon National Park (centered approximately at 36° 56' latitude, 118° 26' W longitude) (Figure 1.1). It is bounded roughly by Taboose Pass, Arrow Peak, Window Peak, and Twin Lakes. This area was delineated into 11 watersheds, six of which drain into the South Fork of the Kings River, four of which drain into Woods Creek, and one of which is an enclosed basin (P watershed, Fig. 1.1). The bedrock of the study area is a complex mixture of large granodiorite masses and metasedimentary rocks, the latter classified as biotite schist, calc-hornfels, marble, and pelitic hornfels and quartzite (Moore 1962).

The study area shows 114 lakes on U.S. Geological Survey 7 1/2' topographic maps (Appendix I). The Synoptic Survey included 104 lakes rather than 114 because 6 were dry or nearly dry, 4 occurred in an enclosed basin at elevations above the known range for aquatic amphibians ($>$ 3650 m, P watershed), one lake (O-19) appeared to be part of another, and one shown as a single lake on the map (F-13) is better described as two (F-13N and F-13S) (Appendix II). The 104 lakes surveyed range from 3130 to 3610 m in elevation, from <0.5 to >10 m in depth, and from approximately 0.1 to 37 ha in area (see Methods in Chapter 4). A few of the smaller lakes present in early summer 1992 had completely dried by late summer. The Synoptic Survey was conducted between 29 June to 4 July 1992.

The 33 lakes sampled in the Detailed Survey represent a subset of the 104 lakes examined during the Synoptic Survey, and were chosen so that the elevation, size, and depths of non-acidic lakes (defined as pH $\geq$ 6.0) matched those for acidic lakes (pH $<$ 6.0). We chose pH 6.0 as the cut-off for delineating acidic vs. non-acidic lakes because previous experimental studies indicated that sensitive taxa begin to decline between pH 5.5 and 6 (Melack et al. 1989, Barmuta et al. 1990). In addition, lakes were chosen so that a reasonable number of lakes containing and lacking fish and breeding amphibians were represented. Acidic lakes were present in 3 of the 11 basins represented in the

Figure 1.1. Study area and designated watersheds. Specific locations and identification of individual lakes are provided in Appendix I. Base map is U.S. Geological Survey 7 1/2' quadrangle, Mt. Pinchot, Calif., Provisional Edition, 1985.


Taboose Pass.
A
B
Striped Mtn.
C
SOUTH FORK KINGS RIVER
D
P
E
Bench Lake
F
Lake Marjorie
Mt. Pinchot
O
Mt. Wynne
Pinchot Pass
Mt. Ickes
L
Arrow Peak
Mt. Perkins
Crater Mtn.
N
WHITE FORK
Pyramid Peak
K
WOODS CREEK
Window Peak
CALIF.
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1 .5 0 1 2
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study area, whereas non-acidic lakes were sampled in 9 of the basins. The Detailed Survey was conducted between 11 August and 1 September 1992.

A subset of 10 lakes was sampled for detailed water chemistry at three times during the summer: during the Synoptic Survey, during the Detailed Survey, and in late summer, 25-26 September (Appendix III). The 10 lakes were chosen to represent a range in pH, with an emphasis on acidic lakes, and because they were among the more accessible lakes in the study area.

PROJECT OBJECTIVES

The specific objectives of the project were the following:

1. Describe the surface water chemistry (pH, acid neutralizing capacity [ANC], electrical conductivity [EC], major ion composition, and aluminum concentrations) in acidic and nearby non-acidic lakes of the Bench Lake/Mt. Pinchot area of the Sierra Nevada.

2. Identify potential sources of acidity for the acidic lakes in this area through an analysis of geological conditions and patterns in water quality data.

3. Determine the distributions of aquatic-breeding amphibians, fish, macroinvertebrates, and zooplankton in relationship to pH.

4. Examine the degree of congruence between the water chemistry associated with presence/absence of organisms in the field and the results of previous experimental and survey studies.

Chapter 2
THE CHEMICAL COMPOSITION OF LAKE WATER FROM THE BENCH LAKE - MT. PINCHOT AREA

Lake water in the Sierra Nevada is characteristically dilute with circumneutral pH and acid neutralizing capacity (ANC) less than 100 $\mu Eq \cdot L^{-1}$ (Melack and Stoddard, 1991). This condition is a result of the combination of a terrain dominated by granitic rocks, thin, acidic soils, and an annual hydrologic cycle dominated by dilute snow melt. Several extensive surveys of Sierra Nevada lakes were conducted in the past decade in an effort to characterize their susceptibility to acidic deposition. The largest of these were the western lakes survey (WLS) conducted by the U.S. E.P.A. (Landers et al., 1987; Eilers et al., 1989), the survey by Melack, Stoddard, and Ochs (1985), and the surveys by G.R. Bradford et al., (unpublished data 1982-1986). Published data have been reviewed and analyzed by Melack and Stoddard (1991). Only one lake in the WLS was found to have a pH less than 6 and 75% of the lakes had sulfate concentrations ($[SO_4]$) less than 10 $\mu Eq \cdot L^{-1}$. Calcium and bicarbonate were the dominant solutes resulting from the well-known rapid weathering reaction of plagioclase abundant in granite (Garrels and MacKienzie, 1967). The outcome of the extensive surveys of the 1980's was that Sierra Nevada lakes are not now acidified, but are vulnerable to the effects of acidic precipitation (Melack and Stoddard, 1991).

The chemical compositions of lakes of the Bench Lake - Mt. Pinchot area are atypical of the lakes sampled in the partially or completely randomized surveys in the 1980's. One of the lakes in the area (C-24 in Appendix I; previously identified as "Lake 45") was sampled repeatedly by G. R. Bradford, but its composition was regarded as anomalous and no further studies were conducted. That lake has a low pH (4.5-5) and high $[SO_4]$ (approaching 1000 $\mu Eq \cdot L^{-1}$) (Gordon Bradford, unpublished data). Several other lakes in the area have been identified that have similar qualities of low pH and high $[SO_4]$. For initially arbitrary reasons, for the purposes of this study, low pH has been defined as pH less than or equal to 6.0. One obvious reason for this choice is that prior to this survey only one or two lakes were reported in the Sierra with pH less than 6. It will be shown that the solution chemistry of SO_4, ANC, and Al also changes in the vicinity of pH 6, making this a reasonable choice for classification purposes.

SELECTION, SAMPLING, AND ANALYSIS OF THE STUDY LAKES

In a preliminary survey of pH and specific conductance, 8 of 104 or about 8% of the lakes sampled in the Bench Lake - Mt. Pinchot area had pH values below 6 (Appendix II). Six of these lakes were resampled for more complete analysis two to three times in 1992: in June/July (n=6), August (n=6), and September (n=5). Five lakes with pH > 6 were sampled at the same times. This 11-lake sample set provides information on seasonal trends in composition. In August samples were collected for 20 additional pH > 6 lakes and 2 additional pH < 6 lakes. Thus, a total of 33 lakes were sampled for analysis of pH, ANC, total Al, Ca, Mg, Na, K, Cl, NO_3, SO_4 and specific conductance. Data are reported below for either the 33 lakes or 31 lakes, because of partial sample loss for two lakes (Appendix III).

Samples were collected by hand from lake outlets (unless otherwise stated) in rinsed polyethylene bottles and were prepared in the field for transportation and storage in three ways. The aliquot for laboratory determinations of pH, conductance, and ANC was simply decanted into deionized (DI) water-leached polyethylene bottles, sealed, and kept cool, 4 °C where possible. The aliquot for Cl, NO_3, SO_4, Ca, Mg, Na, and K was filtered through a 0.45 μm pore-size polycarbonate filter membrane into a DI water-leached polyethylene bottle, sealed and kept cool. The aliquot for total Al was filtered through a 0.1 μm pore-size polycarbonate filter, acidified with purified nitric acid to maintain the solubility of Al, and sealed in an acid-leached, DI water rinsed polyethylene bottle.

Determinations of solutes were conducted by standardized methods using appropriate quality controls (QC) and a predetermined quality assurance plan. Because dissolved Al is labile and has a strong effect on pH, field determinations of pH were conducted on the day of sampling using a glass electrode and the same standards as the laboratory determinations, which were conducted several days later. Specific conductance was also determined in the field as well as the lab, but different QC standards make the results less comparable. The anions, Cl, NO_3, and SO_4, were analyzed using ion chromatography (Dionex AS4A column, sodium bicarbonate eluent). The cations Al, Ca, Na, Mg, and K were analyzed by atomic absorption. For greater sensitivity a graphite furnace was used to atomize Al for atomic absorption analysis.

OVERVIEW OF LAKE WATER COMPOSITIONS

Completed analyses of lake water samples are summarized from Appendix III for 31 lakes (Table 2.1). Field and laboratory conductance values were consistently within 10%, and usually differed by less than 5%. These differences are within reasonable quality limits. The pH values were consistently higher in the field compared with the lab. This difference is certain because of the reproducibility of measurements both in the laboratory and field and the use of identical standards in each location. Analytical variability was less than 1%. Negative ANC in the pH < 6 lake group indicates that some of these lakes have no bicarbonate alkalinity to neutralize the addition of strong acids. Dissolved aluminum hydroxide complexes and colloidal $Al(OH)_3$ are capable of buffering acid additions, however. Measurements of ANC were accurate to less than $\pm 3\ \mu Eq \cdot L^{-1}$ in nearly all determinations. The remaining cations and anions plus ANC were compared for each sample and charge balances were achieved to less than $\pm 15\%$ for all analyses.

The lower pH values measured in the laboratory compared with the field are probably the result of hydrolysis via one of two reactions, Al precipitation (Eq. 2-1), or dissolution of CO_2 from microbial respiration (Eq. 2-2).

$$Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^+ \qquad [2\text{-}1]$$

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \qquad [2\text{-}2]$$

For each μEq of Al precipitating or CO_2 dissolving an equivalent amount of H^+ is produced. Field values for pH are used in this Chapter and Chapter 3 for chemical calculations and comparisons. Total Al samples were acidified to prevent precipitation and should accurately reflect field values. Laboratory pH values are recommended for comparison with data from other lake surveys since the procedures used were similar.

A statistical summary of the lake analyses allows objective comparison of the pH > 6 group lake compositions with pH < 6 (Table 2.2). Comparison of mean and median values within the pH > 6 group indicates that the population of values is skewed. With the exception of pH and Al, median values were lower than mean values. A few large values have a disproportionate influence on the mean. In contrast, the values in the smaller pH < 6 group tended to be more normal in distribution. Mean and median values differed by less and no distinct skewness is evident. Lower standard deviations for the pH < 6 group are also indicative of the similarity in composition

Table 2.1. Analyses of 31 lake water samples from the Mt. Pinchot study area grouped by pH class.

Code	Date	Sp. Cond. Lab	Sp. Cond. Field	pH Lab	pH Field	Al(T)	Cl	NO3	SO4
		--µS/cm--				---------µEq/L----------			
pH > 6 Group									
B-1(2)	15-Aug	26.3	23.7	7.36	7.49	0.97	5.2	5.3	97.8
B-5	15-Aug	5.3	3.1	6.33	6.36	0.95	3.8	1.2	12.7
C-10	13-Aug	22.7	24.7	7.38	7.53	1.10	3.6	1.4	42.3
C-17	13-Aug	22.0	20.0	7.20	7.80	3.16	3.4	1.6	57.2
C-2	1992 (3)	138.1	128.2	7.60	7.99	3.78	8.9	0.3	799.0
C-21	1992 (3)	30.2	27.1	6.78	7.18	1.96	4.3	2.7	173.7
C-23	12-Aug	74.4	62.1	7.10	7.34	1.02	23.5	26.0	367.0
C-4	11-Aug	31.6	26.9	6.83	6.91	2.38	4.1	2.3	178.0
C-5	13-Aug	10.9	12.3	6.90	7.26	0.66	2.7	0.3	22.7
D-4	20-Aug	37.0	34.1	6.72	7.04	5.28	4.2	10.2	232.0
D-5	20-Aug	24.0	21.8	6.46	6.68	2.15	5.5	22.8	119.0
E-1	1992 (3)	17.0	16.5	6.88	7.08	3.95	4.2	1.1	46.1
E-4	20-Aug	9.0	8.8	6.53	6.85	8.73	8.8	0.1	17.5
F-11	1992 (3)	32.7	31.2	6.10	6.41	3.52	6.5	10.4	239.8
F-12	23-Aug	120.8	116.4	7.59	8.61	5.56	7.7	0.2	820.0
F-13S	23-Aug	41.6	40.3	6.62	6.98	3.40	3.7	3.8	273.0
F-4	1992 (3)	17.7	15.7	6.65	7.14	0.93	4.5	0.2	55.5
L-1(2)	30-Aug	13.0	12.2	6.65	6.74	3.26	1.6	1.6	68.3
L-8	30-Aug	52.5	50.1	6.64	6.72	8.43	5.7	9.9	365.0
L-9	30-Aug	54.9	51.7	7.02	6.99	3.68	4.2	11.6	334.0
N-3	24-Aug	33.5	31.2	6.93	7.29	5.08	2.6	0.2	175.0
O-21	24-Aug	15.2	16.0	6.90	7.15	5.95	2.2	0.2	38.5
O-8	24-Aug	29.8	27.9	7.23	7.58	2.72	2.3	0.0	48.0
pH < 6 Group									
C-22	1992 (3)	48.3	42.7	5.48	5.74	47.70	4.4	9.8	372.7
C-24	1992 (3)	56.6	50.7	4.80	5.10	90.47	4.2	12.3	450.0
F-1	1992 (3)	67.3	59.7	5.05	5.34	52.37	5.5	9.3	521.0
F-13N(2)	23-Aug	44.6	42.3	5.71	5.87	7.44	4.7	15.2	343.0
F-14	1992 (3)	30.8	29.0	5.33	5.40	9.91	4.6	25.9	255.0
F-2	1992 (3)	77.2	68.9	4.87	5.16	107.47	4.5	10.0	616.3
L-11	30-Aug	40.4	38.8	5.96	5.99	5.33	7.7	26.2	278.0
L-7	1992 (3)	72.4	68.0	4.77	4.91	86.75	7.3	7.8	540.0

Table 2.1 cont.

Code	Date	ANC	Ca	Mg	Na	K	Na/Ca	[Mg+K]/[Ca+Na]	Mg/K
		μEq/L					mol/mol		
pH > 6 Group									
B-1(2)	15-Aug	116	196	20.3	22.0	10.7	0.23	0.17	0.95
B-5	15-Aug	15	14	3.3	9.1	4.5	1.27	0.38	0.37
C-10	13-Aug	130	189	15.3	11.9	7.9	0.13	0.15	0.97
C-17	13-Aug	99	143	16.7	14.3	8.9	0.20	0.20	0.94
C-2	1992 (3)	303	813	29.0	295.3	10.7	0.73	0.04	1.35
C-21	1992 (3)	64	188	35.7	21.4	7.1	0.23	0.22	2.52
C-23	12-Aug	215	530	35.0	20.5	12.5	0.08	0.11	1.40
C-4	11-Aug	122	216	35.8	24.3	7.1	0.23	0.19	2.52
C-5	13-Aug	56	59	11.0	16.2	6.9	0.55	0.27	0.80
D-4	20-Aug	43	242	15.6	30.0	4.1	0.25	0.08	1.90
D-5	20-Aug	29	162	11.4	20.7	4.9	0.26	0.10	1.16
E-1	1992 (3)	90	111	6.7	24.0	5.7	0.43	0.11	0.59
E-4	20-Aug	44	39	7.4	24.9	6.0	1.26	0.22	0.62
F-11	1992 (3)	15	150	41.2	36.9	17.1	0.49	0.34	1.20
F-12	23-Aug	276	787	104.0	93.0	28.0	0.24	0.16	1.86
F-13S	23-Aug	50	242	41.5	35.0	17.0	0.29	0.24	1.22
F-4	1992 (3)	76	108	9.6	18.2	5.0	0.34	0.14	0.96
L-1(2)	30-Aug	28	73	8.1	17.2	6.3	0.47	0.19	0.64
L-8	30-Aug	49	288	55.0	51.5	18.0	0.36	0.23	1.53
L-9	30-Aug	86	345	54.0	11.4	2.4	0.07	0.16	11.25
N-3	24-Aug	91	199	27.4	59.5	7.8	0.60	0.14	1.76
O-21	24-Aug	77	89	14.7	25.0	7.4	0.56	0.21	0.99
O-8	24-Aug	200	243	21.1	15.9	8.2	0.13	0.14	1.29
pH < 6 Group									
C-22	1992 (3)	4	203	100.3	28.8	10.3	0.28	0.46	4.85
C-24	1992 (3)	-9	196	119.7	27.7	9.0	0.28	0.55	6.67
F-1	1992 (3)	17	248	146.3	47.7	22.3	0.38	0.56	3.28
F-13N(2)	23-Aug	2	193	58.0	51.5	25.0	0.53	0.36	1.16
F-14	1992 (3)	1	150	42.0	28.2	15.4	0.38	0.35	1.37
F-2	1992 (3)	-2	283	168.7	52.3	23.2	0.37	0.55	3.64
L-11	30-Aug	6	216	43.5	40.0	14.8	0.37	0.25	1.47
L-7	1992 (3)	-7	256	114.5	52.3	18.0	0.41	0.42	3.18

Table 2.2. Statistical summary of water quality data from the Mt. Pinchot study area grouped by pH class.

	Sp. Cond. Lab	Sp. Cond. Field	pH Lab	pH Field	Al(T)	Cl	NO3	SO4
	--μS/cm--				---------μEq/L----------			
pH > 6 Group								
Mean	37.4	34.9	6.89	7.18	3.42	5.4	4.9	199.2
Std. Dev.	32.6	30.4	0.38	0.50	2.22	4.3	7.1	218.6
n	23	23	23	23	23	23	23	23
Median	29.8	26.9	6.88	7.14	3.26	4.2	1.6	119.0
Low	5.3	3.1	6.10	6.36	0.66	1.6	0.0	12.7
High	138.1	128.2	7.60	8.61	8.73	23.5	26.0	820.0
pH < 6 Group								
Mean	54.7	50.0	5.25	5.44	50.93	5.4	14.6	422.0
Std. Dev.	15.4	13.5	0.42	0.36	38.26	1.3	7.0	122.3
n	8	8	8	8	8	8	8	8
Median	52.4	46.7	5.19	5.37	69.09	4.7	11.2	411.3
Low	30.8	29.0	4.77	4.91	5.33	4.2	7.8	255.0
High	77.2	68.9	5.96	5.99	107.47	7.7	26.2	616.3

	ANC	Ca	Mg	Na	K	Na/Ca	$\frac{[Mg+K]}{[Ca+Na]}$	Mg/K
	----------μEq/L----------					-----mol/mol-----		
pH > 6 Group								
Mean	99	236	26.9	39.1	9.3	0.41	0.18	1.69
Std. Dev.	77	205	22.1	57.6	5.7	0.32	0.08	2.11
n	23	23	23	23	23	23	23	23
Median	77	189	20.3	22.0	7.4	0.29	0.17	1.20
Low	15	14	3.3	9.1	2.4	0.07	0.04	0.37
High	303	813	104.0	295.3	28.0	1.27	0.38	11.25
pH < 6 Group								
Mean	2	218	99.1	41.1	17.2	0.38	0.44	3.20
Std. Dev.	8	40	44.4	10.6	5.6	0.07	0.11	1.79
n	8	8	8	8	8	8	8	8
Median	1	209	107.4	43.8	16.7	0.37	0.44	3.23
Low	-9	150	42.0	27.7	9.0	0.28	0.25	1.16
High	17	283	168.7	52.3	25.0	0.53	0.56	6.67

found in the low pH lakes compared with the pH > 6 lakes. The two populations of lakes are compared on the basis of their median composition values. As expected, [SO_4] was higher in the low pH lakes and ANC was lower. The mean ANC of the pH < 6 lakes is not significantly different from 0. Higher [Al] and specific conductance in the low pH lakes is easily explained as a response of Al and other mineral solubility to pH. Mean and median [Cl] were similar in both groups. Nitrate was higher in the low pH lakes. Median concentrations of base cations Mg, Na, and K were higher in the low pH lakes, but [Ca] means and medians were about the same in both groups.

It is useful to compare the lakes in this survey with the WLS (Melack and Stoddard, 1991). The pH < 6 lakes in this survey amounted to more than 25% of the sample population while only one lake with pH less than 6 was chosen by the random selection methods of the WLS. More than 75% of the lakes in this survey had ANC values less than 100 $\mu Eq \cdot L^{-1}$ compared with 65% in the WLS. In the WLS 75% of the lakes had [SO_4] less than 10 $\mu Eq \cdot L^{-1}$. In this survey 100% of the lakes had [SO_4] greater than 10 $\mu Eq \cdot L^{-1}$. Comparing only the pH > 6 lakes with the WLS, median values for all but [Cl], [Na], and [K] were lower in the WLS, except for pH, which was slightly higher. The entire population of lakes in this survey is distinctly different from "typical" high-elevation Sierra Nevada lakes. Lake pH is only one indicator of these differences, [SO_4], [Ca], [Mg], and [NO_3] are also prominent.

Based on the WLS, typical dilute lakes in the Sierra Nevada are classified as Ca-Na-HCO_3 dominated waters as a consequence of plagioclase weathering (Melack and Stoddard, 1991). Relative dominance was based on equivalent concentrations. As lake waters become less dilute, they become Ca-HCO_3-SO_4 or Ca-Mg-HCO_3 waters depending on whether pyrite or metavolcanic influences are inferred, respectively (Melack et al., 1985; Melack and Stoddard, 1991). This survey found several classes not previously identified in high-elevation Sierra Lakes. Eleven of the 23 lakes in the pH > 6 group (Table 2.1) are Ca-SO_4-HCO_3 lakes. Five of the low pH lakes are Ca-Mg-SO_4 lakes and the remaining 3 are Ca-Na-SO_4 dominated. A total of 19 lakes in this survey have SO_4 as the dominant anion. To round out this peculiar assemblage of lakes, three lakes high in Na were identified (C-2, B-5, and E-4). In each of these lakes on at least one occasion the molar ratio of Na:Ca was greater than 1.

RELATIONSHIPS AMONG DISSOLVED CONSTITUENTS

The patterns of variation of several parameters with pH in the lakes of the Bench Lake - Mt. Pinchot area makes pH 6 a logical criterion for classification. The ANC

values determined for all samples (including duplicates and triplicates for some lakes) plotted against pH show that at about pH 6, ANC approaches 0 $\mu Eq \cdot L^{-1}$ (Fig. 2.1). This is simply a consequence of the relationship between ANC and alkalinity in these waters, a measure of dissolved carbonate (CO_3) and bicarbonate (HCO_3) (Stumm and Morgan, 1981). The definition of ANC is the difference between the sum of the strong bases or base cations (C_B) and the sum of the strong acids or acid anions (C_A) (Eq. 2-3).

$$ANC = C_B - C_A \qquad [2\text{-}3]$$

This relationship is demonstrated for the Bench Lake - Mt. Pinchot lakes by plotting titrated ANC versus C_B-C_A (Fig. 2.2). Above ANC = 0 $\mu Eq \cdot L^{-1}$, deviations from the 1:1 line indicate the presence of dissolved species which have not been factored into the C_B or C_A. These could include organic anions, molybdates, or borates, which would result in values below the 1:1 line or cations such as Li, Sr, Al, Fe, and Mn which would give values above the 1:1 line. Near ANC = 0, $C_B = C_A$. As acidity increases, additional cations (e.g., Al, Fe) become soluble enough to cause $C_B < C_A$ (consequently $C_B - C_A < 0$. Below ANC = 0 acidic anions are balanced in solution by dissolved cations other than Ca, Mg, Na, and K which are usually the dominant base cations. For those lakes between pH 6 and 7.5, C_B is statistically independent of pH (which means a line drawn through the points in Fig. 2.3 would be flat). The relationship between ANC and pH (Fig. 2.1) indicates that $C_B - C_A$ increases over the same pH range, hence, C_A must be increasing as pH decreases. It is strong acids in these lake-watersheds which titrate ANC to 0, not differences in the base cation composition. Below pH 6, there is an apparent increase in C_B as pH decreases (Fig. 2.3). This is due to a increase in solubility of minerals at lower pH.

The presence of high concentrations of SO_4 in the lakes indicates that sulfuric acid (H_2SO_4) is the acid responsible for the low ANC and pH of the low pH lakes. The log[SO_4] increases as pH decreases below pH 6 (Fig. 2.4). Above pH 6, log[SO_4] is independent of pH, a consequence of ANC titration of SO_4 acidity. It is interesting to note that the highest SO_4 concentrations were at high pH (Lakes C-2 and F-12). Both Cl and NO_3 are also strong acid anions and the latter is under study as an important airborne pollutant (CARB, 1992). Median [NO_3] is higher in the low pH lakes, but this relationship is not a strong function of pH (Fig. 2.5). There is a distinct difference between the group of pH > 6 lakes and the low pH lakes. In many cases, [NO_3] in the former group approaches 0 $\mu Eq \cdot L^{-1}$ while none of the low pH lakes had [NO_3] less than 6 $\mu Eq \cdot L^{-1}$, which is 20 times the WLS median. Biological activity may be an important

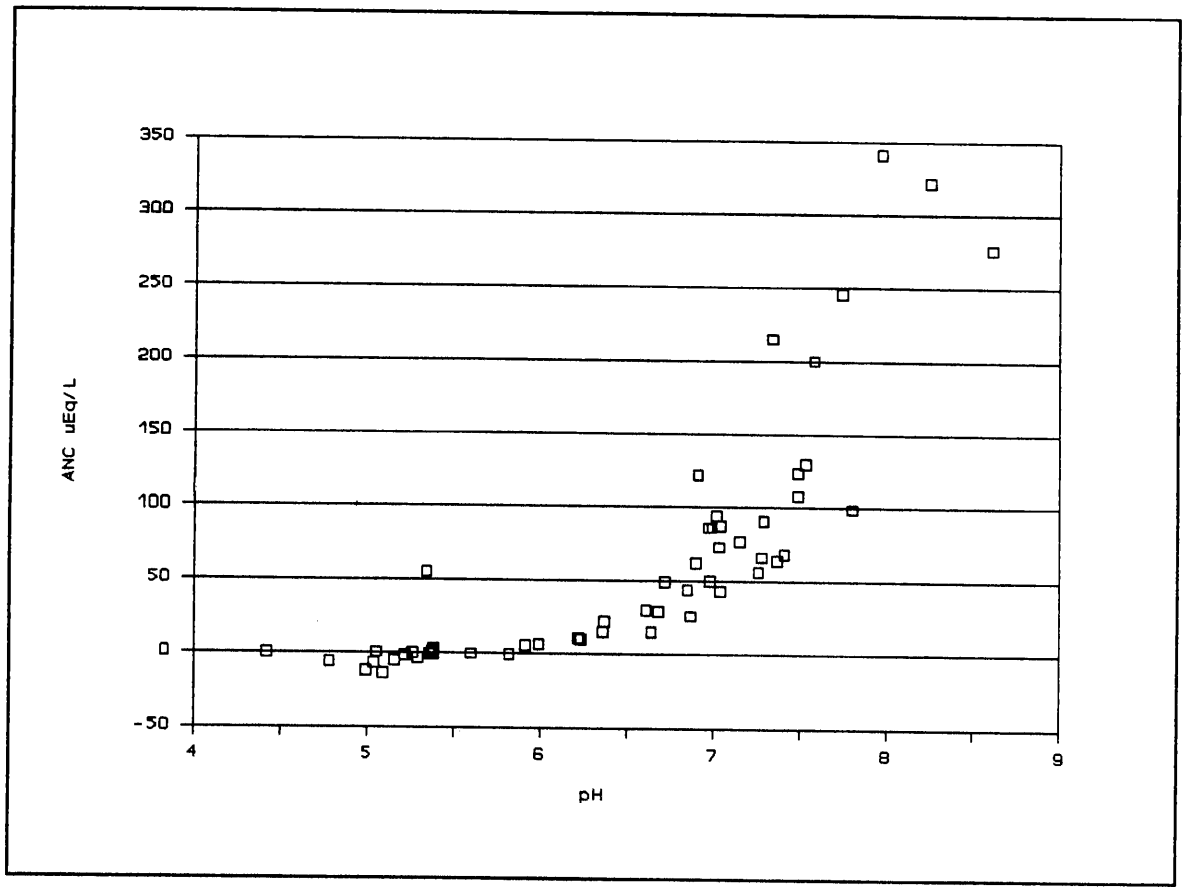


Figure 2.1. Acid neutralizing capacity of lake samples versus lake pH.

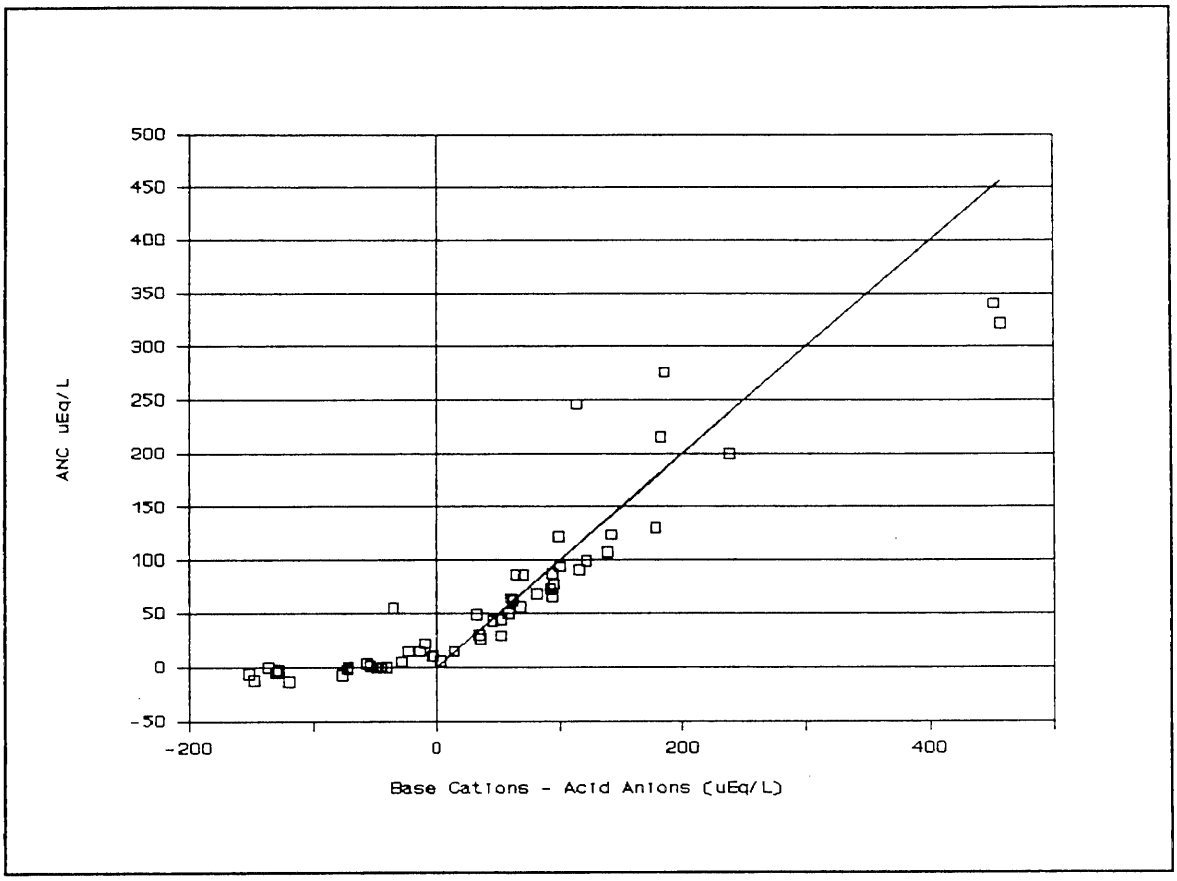


Figure 2.2. Comparison of measured ANC values for all lake samples with the difference between sum of base cations and (C_B) and sum of acid anions (C_A).

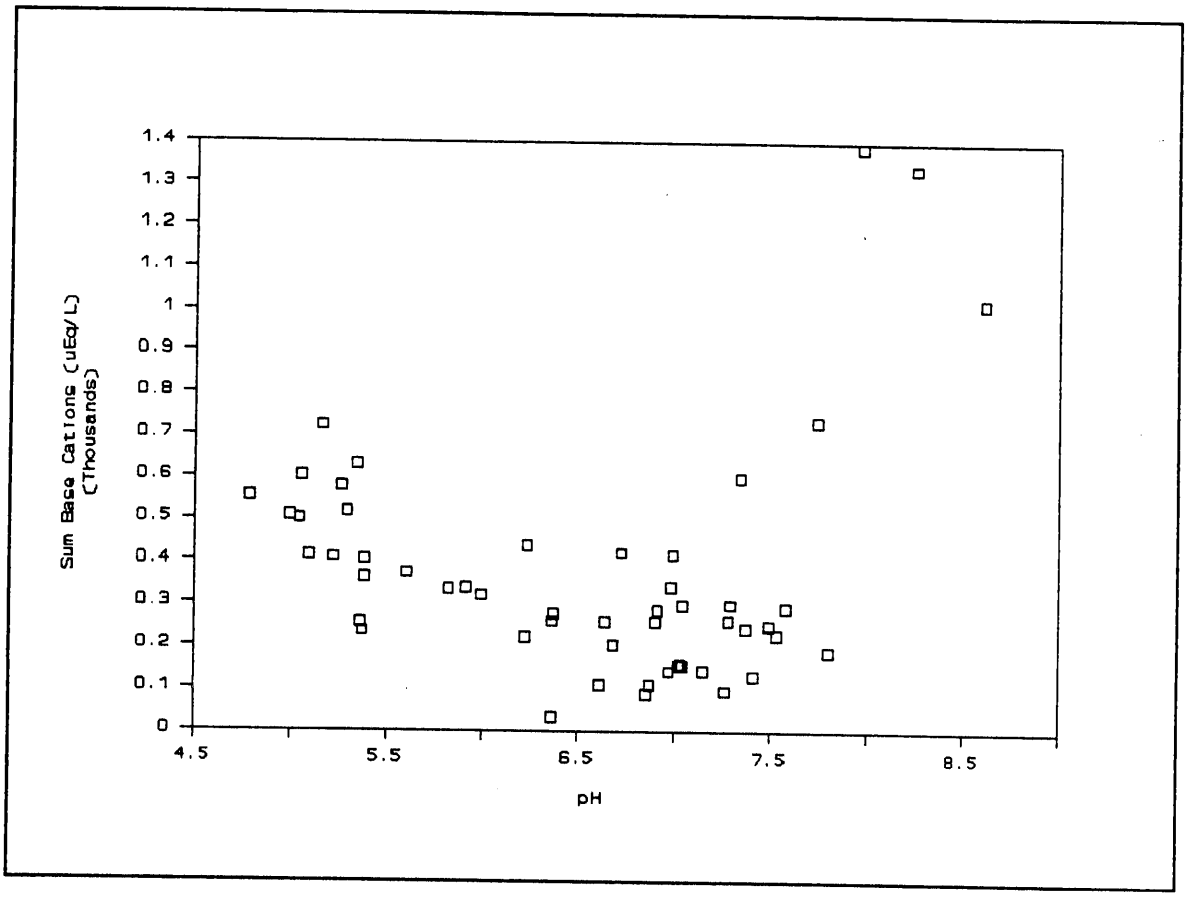


Figure 2.3. Sum of base cations of lake samples versus lake pH.

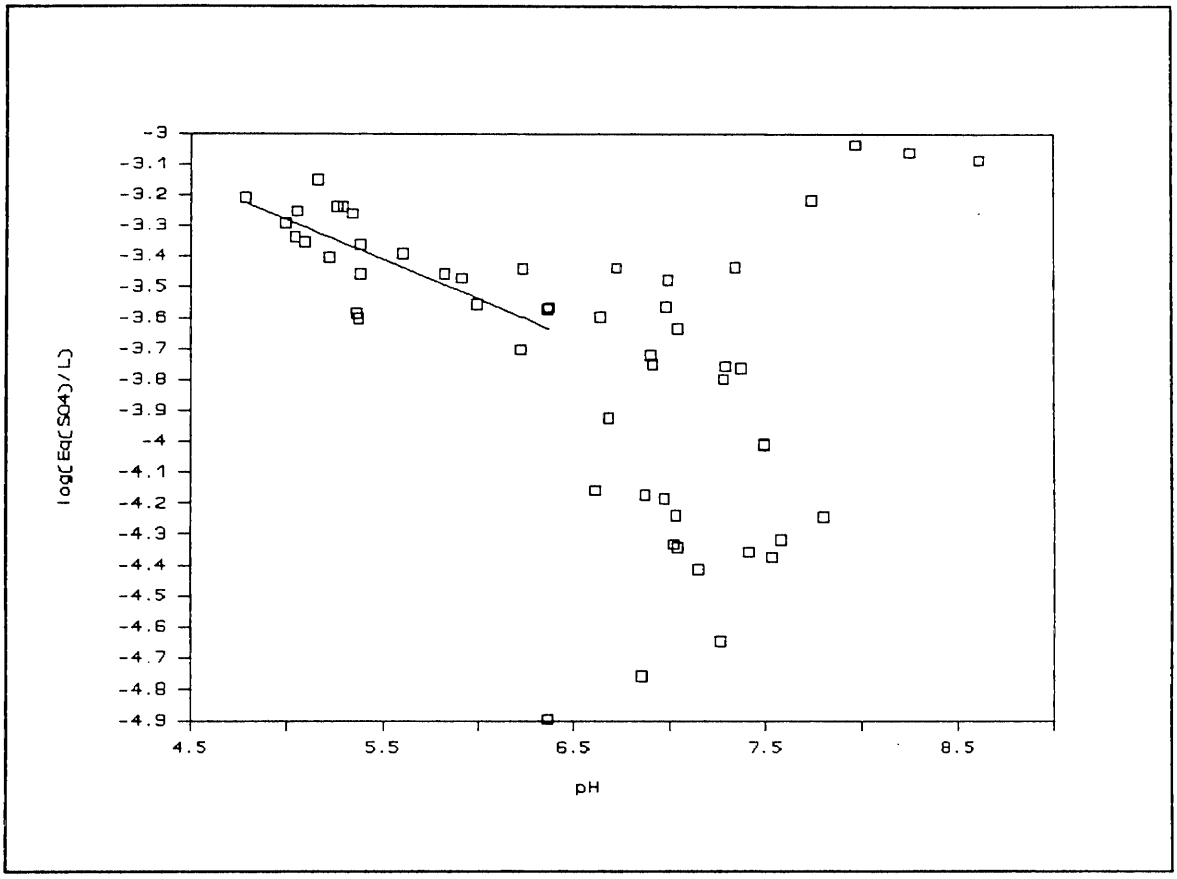


Figure 2.4. Sulfate concentrations of lake samples versus lake pH.

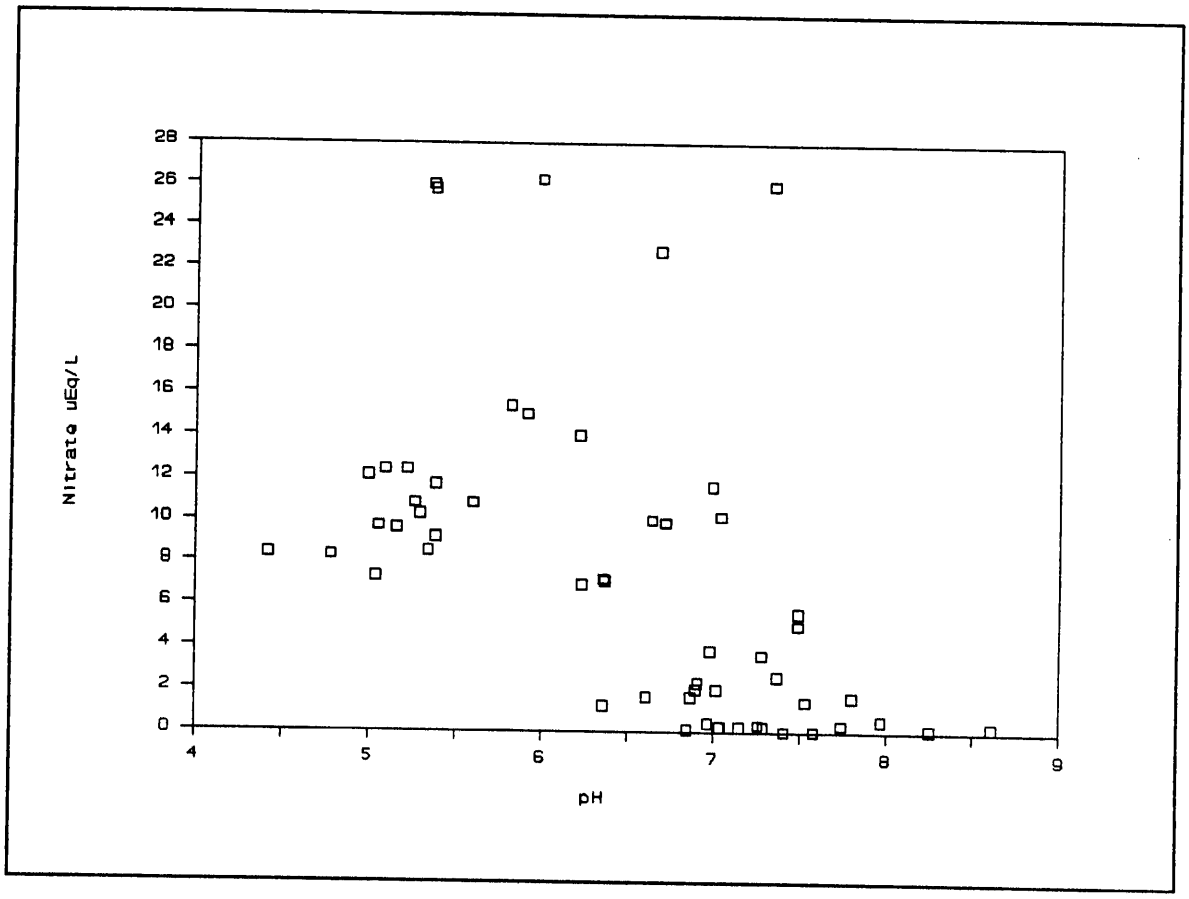


Figure 2.5. Lake nitrate concentrations versus lake pH.

factor in control of $[NO_3]$ with low pH, low productivity lakes consuming less NO_3. A final check on strong acids finds that [Cl] is independent of pH, as expected if the source is uniform deposition of non-acid marine aerosols and Cl is a conservative anion in these watersheds (Fig. 2.6). Deviations from the median [Cl] of about 4.5 $\mu Eq \cdot L^{-1}$ should be a result of dilution by snow melt or evaporative concentration. The latter may be a factor for lake C-23, which had exceptionally high [Cl], more than 5 times the median concentration. Lake C-23 has no apparent outlet and also has higher $[SO_4]$, $[NO_3]$, and [Ca], which may accumulate in a similar manner.

An inevitable consequence of lowered pH is the increase in solubility of Al (Fig. 2.7). The slope of the log[Al]-pH relation below pH 6.5 is -1.12 ± 0.24 which is not significantly different from the stoichiometry of 1 equivalent of Al per equivalent of H. This describes the hydrolysis of Al to $Al(OH)_3$ (Eq. 2-1), which may precipitate as a mineral such as gibbsite. This is an important reaction for non-HCO_3 buffering of low-pH natural waters which will be addressed in Chapter 3. Above pH 6.5, [Al] is independent of pH. Log[Al] is correlated with $\log[SO_4]$ above $[SO_4]$ of about 150 $\mu Eq \cdot L_{-1}$ (Fig. 2.8). This may be a result of SO_4-acidity.

The use of pH 6 for a criterion for classification of low pH lakes is further justified by several observations. Below pH 6, the ANC of these lakes is essentially independent of pH. Sulfate concentrations increase with increasing acidity below pH 6, while they are independent of pH above pH 6. Aluminum follows a similar pattern. Finally, nitrate concentrations are also consistently higher below pH 6. These criteria have some physical-chemical basis, but their main utility is for this particular data set, in which these patterns can be observed.

SEASONAL TRENDS IN LAKE WATER COMPOSITION

Like other Sierra lakes, 9 of the 11 lakes sampled 2-3 times during the summer of 1992 were clearly recovering from the dilution which occurs every spring in response to snow melt (Melack and Stoddard, 1991; Williams and Melack, 1991). This was evident from increasing specific conductance, [Ca], [Mg], and $[SO_4]$ over the season. The trend in field pH, however, was downward, especially in the low pH lakes. This could be in response to hydrolysis and precipitation of Al mobilized during snow melt, or, more likely, it may be a result of decreased dilution of acidic sources within the lake-watershed basins. Evidence for the latter is the decrease in ANC observed in the low pH lakes as the summer progressed.

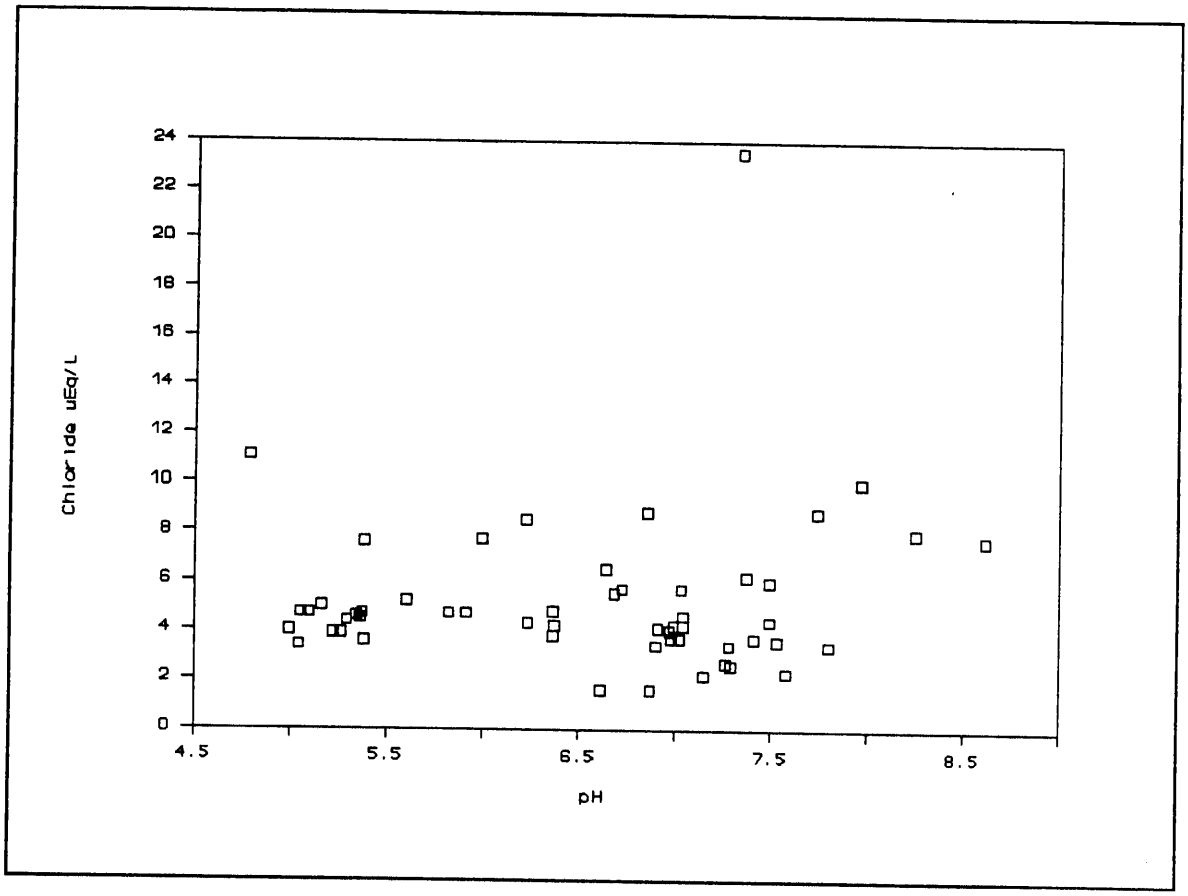


Figure 2.6. Lake chloride concentrations versus lake pH.

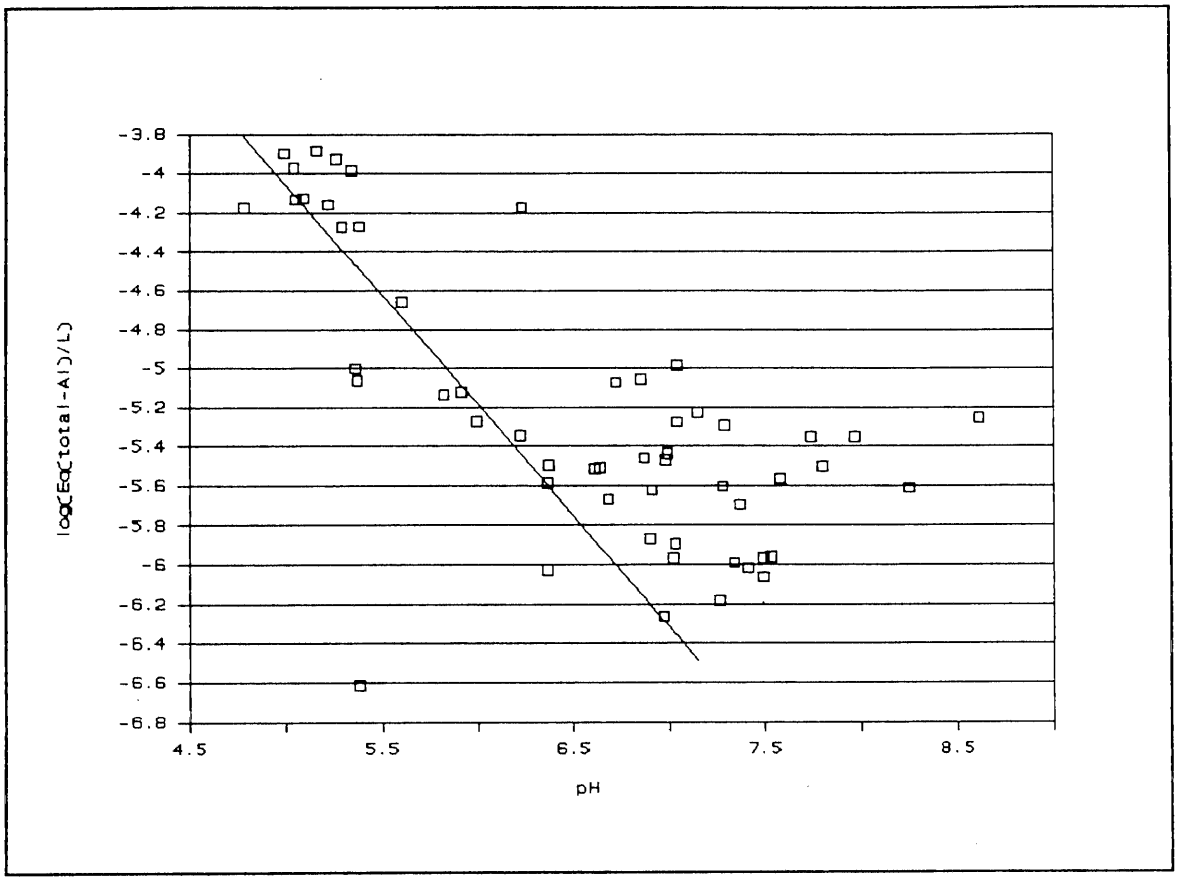


Figure 2.7. Lake total aluminum concentrations versus lake pH.

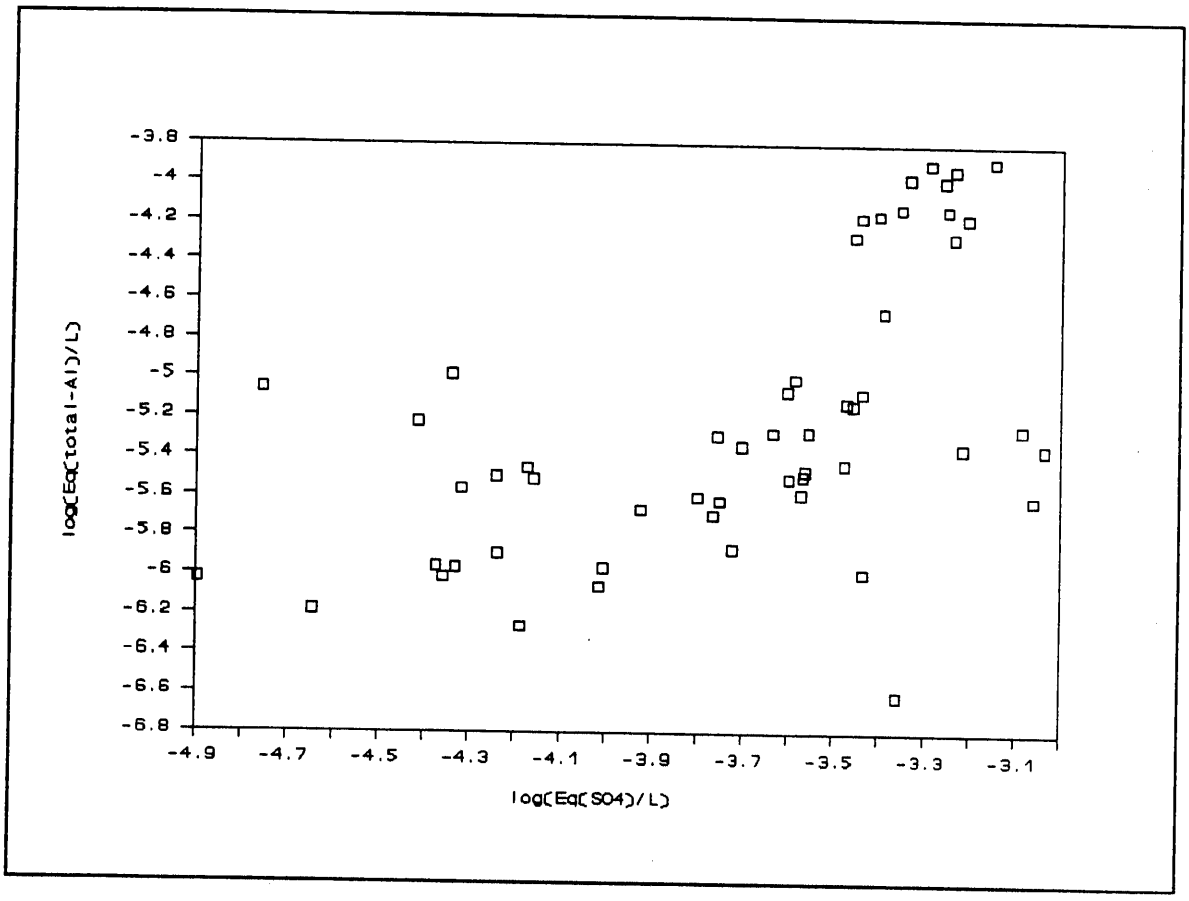


Figure 2.8. Lake total aluminum concentration versus sulfate concentration.

LAKE COMPOSITION AND INFERRED MINERAL WEATHERING

The analysis of the composition of Sierra Nevada runoff by Feth et al. (1964) and Garrels and MacKienzie (1967) provides a model for additional interpretation of lake composition data from the Bench Lake - Mt. Pinchot area. Pyrite was identified as the most likely source of sulfate, which is normally only a minor component in Sierran waters. However, pyrite is present in significant quantities in this area (Moore, 1963; Mahood and Gansecki, Appendix IV) and the dominance of the anion composition of 19 of the lakes by SO_4 is an indication of the importance of this mineral in controlling lake water composition.

The Na:Ca ratio is hypothesized to be dependent on the plagioclase found in the surrounding granite, typically between 0.60 and 0.74 in the Sierra (Garrels and MacKienzie, 1967). The mean molar ratio of Na:Ca is similar for the two lake pH groups, near 0.4 (Table 2.2). This is low compared with typical plagioclase values, however, additional sources of Ca, including calcite, may result in lower than expected ratios. The overall consistency of the Na:Ca ratio is suggestive of a common weathering source in all but a few of the more alkaline lake-watersheds studied.

The proportion of {[Mg]+[K]}/{[Ca]+[Na]} is "typically" approximately 0.2 because of the relatively low amounts of mafic minerals in granite and the lower weathering rate of K-feldspar compared with plagioclase (Garrels and MacKienzie, 1967). The pH $>$ 6 group follows this pattern, but the low pH group has a mean ratio of 0.44. Likewise the median Mg:K ratio of the pH $>$ 6 group is 1.2, which is similar to the expected ratio of 1, while the ratio for the low pH lakes is a much higher: 3.2. The differences in these values indicate that mafic minerals play an increasingly important role in determining the composition of lake waters as the pH decreases. What cannot be seen from the lake composition data alone is the relationships among the inferred causative agents. For example, it is not possible to tell whether the increased [Mg] at lower pH is a result of greater aggressiveness of acidic waters toward mafic minerals or if mafic minerals are directly associated with the pyrite which is also the source of acidity. More information on watershed mineralogy and hydrology is needed to fully address the question of the sources of acidity and cations in these lake waters. This problem is addressed in Chapter 3.

SUMMARY

Lake water composition data for 33 lakes in the Bench Lake - Mt. Pinchot area of the eastern Sierra Nevada indicate that these lakes are all unusual in comparison to typical Sierra Nevada lakes sampled in previous surveys. Unlike typical Ca-Na-HCO_3-dominated Sierra lakes, SO_4 concentrations are high enough to classify 19 of these lakes with SO_4 as the dominant anion. Furthermore, 25% of the lakes surveyed had pH values less than 6 and essentially 0 ANC. The source of the SO_4 is the highly acidic oxidation products of pyrite weathering. The effect of the H_2SO_4 has been to titrate the ANC of various lakes by different amounts, presumably depending on the amount of pyrite present in each watershed. Below pH 6, increased H_2SO_4-acidity resulted in increased concentrations of Al, sum of base cations, and NO_3. Increased mineral solubilities explain the Al and base cation trends, but the reason for the NO_3 trend is not as clear. Increased Mg in more acidic lakes is an indication of increased weathering of mafic minerals, but it is ambiguous whether this is a consequence of acidification or merely an association with the presence of pyrite.

Chapter 3
GEOCHEMISTRY OF WATERSHED ACIDIFICATION IN THE BENCH LAKE/MT. PINCHOT AREA

SURFICIAL GEOLOGY: BRIEF SUMMARY OF FINDINGS

The Mt. Pinchot area was the subject of a reconnaissance survey for major geologic features over 30 years ago (Moore 1963) That survey noted the great variety of lithologies in the area, mostly granitic, but also some metamorphic. A pyrite-containing alteration zone was identified 1 mile west of Crater Mt., in the headwaters of the White Fork, our basin L (Fig. 1-1; Appendix I). Previous lake surveys found acidic waters in the C basin (C-24 [Appendix I], previously "Lake 45", G. R. Bradford, unpublished data), and the F basin (Bradford et al. 1993; Jenkins and Kratz, unpublished). The mapped extent of the pyrite-rich rocks did not seem to correspond to the occurrence of acidic rocks, hence, the geology of the area was surveyed in greater detail as a part of the present study (Mahood and Gansecki, Appendix IV).

The 1992 geological survey established the presence of several bands of hydrothermal alteration of metamorphic rocks in the F, L, C, O, and N drainages (Mahood and Gansecki, Appendix IV). These appear to be the principal areas rich in exposed pyrite, although it was observed as an accessory in granite as well. This confirmed the suspected correspondence between acidic lakes and pyritic outcrops, which act as point-sources of acidity, similar to acid-mine drainage. Other geological sources of acidity were not found (e.g., volcanic, hydrothermal), and lake acidification is so localized that acidic deposition is also not a factor. It was clear, however, that the presence of pyrite was not sufficient to predict lake acidification. Other features, such as the rock glaciers in basins C and F, and a fault zone in the F drainage, play an important role in mechanical breakdown of the rocks, increasing their production of acidity out of proportion to their apparent extent. Basin hydrology further affects the amount of surface water acidification that occurs by limiting the contact time with acid-producing and acid-neutralizing rocks.

CORRESPONDENCE BETWEEN LITHOLOGY AND LAKE COMPOSITION

The survey of the composition of lake waters in the Bench Lake/Mt. Pinchot area identified 8 lakes in the Detailed Survey that are acidic, with an arbitrarily-defined pH 6 or less (Chapter 2). None of the lakes surveyed for major anions and cations had sulfate

concentrations ([SO_4]) less than or equal to the western lakes survey median of 7 $\mu Eq \cdot L^{-1}$ (Melack and Stoddard, 1991). Sulfate was the dominant anion (exceeding bicarbonate, HCO_3) in 19 of the 33 lakes analyzed. The SO_4-dominated, acidic lakes were clustered in 3 adjacent watersheds: C, F, and L (Fig. 1-1; Table 2.1). In addition, watersheds D and N had lakes with anion compositions dominated by SO_4 (Table 2.1).

The acidic lakes in the C drainage are C-22 and C-24. Four acidic lakes, F-1, F-2, F-13N, and F-14, were identified in the F drainage. A meadow upstream from lake F-2 is also acid-affected. The remaining acidic lakes were L-7 and L-11. Five of the eight acidic lakes and a meadow were directly affected by zones of pyrite-rich hydrothermally-altered metamorphic rock. Lakes C-24, F-13N, F-14, L-7, L-11, and the meadow in the lower F-drainage fall into this class of surface waters directly affected by pyrite. The rest of the acidic lakes were located on rocks much lower in pyrite content, but drainage from other areas caused them to still be acidic.

Two other classes of acid-affected lakes are present: 1) lakes acidified or high in SO_4 because they receive drainage from lakes directly affected by pyrite-rich outcrops, and 2) lakes in close proximity to pyrite-rich outcrops that are not acidic but are high in SO_4, indicating that they are acid-affected. The influence of acidic drainage is so great that lake composition along transects of over 2 km were affected. Below the acidic C-22, which is directly affected by C-24, lakes C-21, C-23, and C-4 anion compositions are still dominated by SO_4. Likewise, drainage from the meadow above F-2 has a strong influence on both lakes F-2 and F-1. Lakes F-11, F-12, and F-13S, all dominated by SO_4, are also influenced by drainage from adjacent acidic lakes. The acid-affected lakes C-2, L-1, L-8, L-9, and N-3 have high [SO_4], clearly associated with adjacent altered granitic (L-1) or metamorphic rocks (L-8, L-9, N-3) or unaltered metamorphic rock (C-2). However, these basins have weathering rates of non-pyritic minerals sufficiently high to neutralize pyrite oxidation, thus raising their pH to circumneutral. Thus, although these lakes did not appear to be acid-affected based on pH alone, their anion composition indicates a direct effect of pyrite-rich bedrock. Overall, the relationship between acid-affected lakes and bedrock lithology is consistent for the area studied.

GEOCHEMISTRY OF ACID PRODUCTION IN THE BENCH LAKE/MT. PINCHOT AREA

The production of acidity from pyrite oxidation is a well-known biogeochemical process (Nordstrom, 1982; Brown and Jurinak, 1989). The overall process is summarized by the reaction:

$$FeS_2(s) + (15/4)\ O_2(aq) + (7/2)\ H_2O \rightarrow Fe(OH)_3(s) + 2\ H_2SO_4(aq) \qquad [3\text{-}1]$$

This reaction is usually catalyzed by acidophilic thiobacilli but can occur in their absence provided that sufficient water and oxygen (or oxidized iron) are present. Oxidation of 0.5 grams of pyrite (about a "pinch") produces over 8 meq of sulfate. This is approximately equivalent to the mean annual deposition on a square meter in Los Angeles of 6-8 meq·m^{-2} of non-seasalt sulfate measured by ARB from 1984 to 1990 (CARB, 1992). The effects of acidity generated by pyrite are evident in two ways in the Bench Lake/Mt. Pinchot area: 1) surface water chemistry is altered by sulfuric acid and several lakes and water courses are acidic, and 2) secondary mineral products have formed which are unique to acid-sulfate weathering.

The effect of sulfuric acid on surface water composition has been described (Chapter 2). The range in compositions of lakes which have been acidified form a continuous series with the compositions of lakes which have not been acidified but have been altered to the point that anion composition is dominated by [SO_4] (Fig. 2.2). This series is described by the titration of acid neutralizing capacity (ANC) by H_2SO_4, where ANC = C_B - C_A or the difference in the sum of base cations (C_B) and sum of acid anions (C_A), the latter dominated by SO_4. Below pH 6, the solubility of Al increases in proportion to the decrease in pH (Fig. 2.7). This solubility relation can be further refined by the use of thermodynamically-based solubility equilibrium modelling.

The well-known chemical model WATEQ4F (Ball and Nordstrom, 1991) was used to compute the activity of Al^{3+} (abbreviated here as $\{Al^{3+}\}$) in the lake waters studied. The Al^{3+} activity is directly related to the solubility of various minerals and is usually thought of as corresponding to the most labile fraction of dissolved aluminum, free of complexation with organic or inorganic anions. The relationship between $\{Al^{3+}\}$ and pH is well defined (Fig. 3.1). The WATEQ4F model compares calculated $\{Al^{3+}\}$ with the solubility of various minerals, of which three appear to be relevant to the solution chemistry of waters in this area: amorphous aluminum hydroxide, $Al(OH)_3$ (a), gibbsite (also with the formula $Al(OH)_3$, but more crystalline), and jurbanite, $AlOHSO_4$. Basaluminite ($Al_4(OH)_{10}SO_4$) and jarosite do not appear to be related to Al or SO_4 solubility in lake waters although they may be important in soils or springs.

Gibbsite and $Al(OH)_3$ (a) have similar solubility relations except that $Al(OH)_3$ (a) is much more soluble than gibbsite. The proportion of {Al} released in response to H consumed is 1:3 on a molar basis (Eq. 3-2, 3-3) for both minerals.

$$Al(OH)_3\ (a) + 3\ H^+ = Al^{3+} + 3\ H_2O \qquad [3\text{-}2]$$

$$Al(OH)_3 \text{ (Gibbsite)} + 3\ H^+ = Al^{3+} + 3\ H_2O \qquad [3\text{-}3]$$

$$AlOHSO_4 + H^+ = Al^{3+} + SO_4^{2-} + H_2O \qquad [3\text{-}4]$$

The proportion of $\{Al^{3+}\}$ released by jurbanite is 1:1 with respect to H consumed (Eq. 3-4). The solubilities of these three minerals can be compared by plotting the theoretical $\{Al^{3+}\}$ in equilibrium with each mineral over the same range of pH (Fig. 3.1). The same thermodynamic data contained in WATEQ4F were used to make these calculations. It is difficult to directly compare jurbanite solubility with the $Al(OH)_3$ minerals in a 2-dimensional plot because of the added variable of $\{SO_4^{2-}\}$. To accommodate this problem solubility boundaries are plotted for the minimum (10^{-5}) and maximum ($10^{-2.5}$) $[SO_4]$ concentrations measured (Fig. 3.1). Above pH 6, jurbanite is more soluble than $Al(OH)_3$, but under more acidic conditions, their solubilities are similar.

From the equilibrium diagram, it is apparent that over most of the pH range observed $\{Al^{3+}\}$ is related to $Al(OH)_3$ solubility (Fig. 3.1). Below pH 6, $\{Al^{3+}\}$ may be related to jurbanite solubility, particularly in lakes C-22, C-24, F-1, F-2, and L-7. Solubility computations for samples from each of these lakes support this conclusion. Further support for the identity of jurbanite as the solid phase controlling Al and SO_4 solubility is the energy dispersive x-ray spectrometry analysis (EDS) of the white precipitate found on rocks in the C, F, and L watersheds (Mahood and Gansecki, Appendix IV). This precipitate is so pervasive and brilliant that is visible along the banks of the White Fork (basin L) from a great distance. The EDS analysis indicates that Al and S are major elemental components of the precipitate and that Si and Fe are not. This test cannot detect OH. These results correspond with the composition of jurbanite, or, possibly, a mixture of jurbanite and $Al(OH)_3$ (a). Analysis of the same precipitate by x-ray diffraction (Mahood and Gansecki, Appendix IV) is inconclusive since the results only indicate that it is x-ray amorphous. The presence of jarosite in the meadow in the F-drainage (Mahood and Gansecki, Appendix IV) is consistent with very acidic conditions caused by pyrite oxidation, however this mineral was not identified in the vicinity of the lakes downstream, therefore, it may not have a direct effect on SO_4 solubility in surface waters.

Solubility equilibria and mineralogical data verify that jurbanite solubility controls Al and SO_4 in at least 5 of the acidic lakes. This provides sufficient evidence to complete the geochemical description of the acidifying process for the affected lakes in the Bench Lake/Mt. Pinchot area. Where pyrite is exposed to air and water, oxidation (Eq. 3-1) generates sulfuric acid. Part of this acid is consumed in the decomposition of

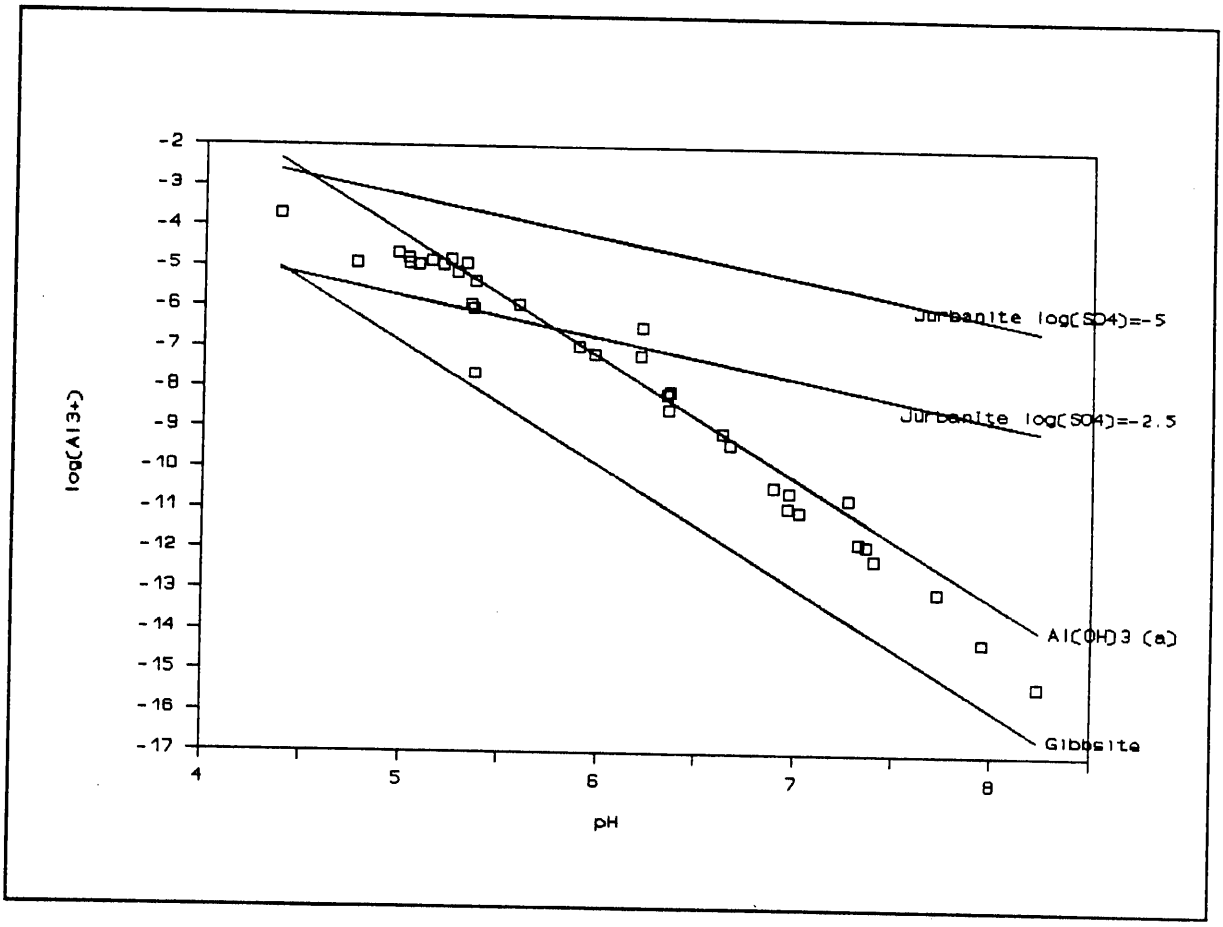


Figure 3.1. Solubility relations for amorphous aluminum hydroxide ($Al(OH)_3$ (a)), gibbsite, and jurbanite compared with Al activity for the study lakes.

feldspars, amphiboles, and biotite associated with the granitic and metamorphic rocks where the pyrite is found. This produces the high levels of dissolved Ca and Mg found in the acidic and acid-affected lakes (Table 2.1). Under conditions where transport of weathering products is minimal, acidification becomes intense enough for the formation of jarosite by precipitation from solution (Bladh, 1982). This explains the presence of jarosite in the meadow in the F-drainage. When the pH is higher and transport greater, goethite precipitates, leaving an acidic solution rich in Al, SO_4, and base cations. As this solution travels downstream, neutralization of solution pH leads to the precipitation of jurbanite and $Al(OH)_3$ (a). Precipitation of these minerals does not remove them from influence on surface water chemistry. When surface water pH, [SO_4], or [Al] change, jurbanite or $Al(OH)_3$ (a) may dissolve to maintain relatively stable concentrations of these solutes. Thus, pH and solution composition may be buffered by solubility equilibria in the most acid lakes and drainages.

Another application of solubility equilibria to lake water composition in this area is the influence of calcite ($CaCO_3$) on pH, [Ca], and ANC in lakes C-2 and O-8. Using the acid test, precipitated $CaCO_3$ was found in springs along the margins of C-2. Calculations using WATEQ4F verified that the pH, [Ca], and ANC were consistent with calcite solubility. In these lakes, a change in pH would lead to the dissolution or precipitation of $CaCO_3$. This may help explain why C-2 remains a neutral pH lake in spite of having the second highest average [SO_4] among the lakes surveyed. In this case, intense acid production is very effectively neutralized by calcite dissolution. Neither pyrite nor calcite were obvious in the metamorphic rocks adjacent to lake C-2, however, this is the likely source of both minerals.

ACIDIC LAKES IN THE BENCH LAKE/MT. PINCHOT AREA AS MODELS FOR THE EFFECTS OF ACIDIC DEPOSITION ON SIERRA NEVADA LAKES

One concern of the Atmospheric Acidity Protection Program (AAPP) is what effects acidic deposition may have on the Sierra Nevada. At this site in the eastern Sierra a condition exists where natural acidification is occurring in a terrain otherwise representative of the range. The nature of acidic deposition is that its spatial distribution should be approximately even at this distance from the source. This is in contrast to the observed acidic drainage derived from pyrite oxidation which is essentially point-source. The effects of this difference on the utility of this site as a model for the effects of acidic deposition are best understood by examining the hydrologic system of lakes and streams observed.

Water appears to be the determining reactant in production of acidity in the Mt. Pinchot area. Acidic springs were found in each of the three watersheds containing acid-affected lakes. In the C and lower F drainages springs were fed by melt water from rock glaciers on the north-facing walls of the drainages (Appendix I). In the south-facing L and west-facing upper F drainages acidic springs were found, but they were fed by groundwater seepage from lakes and talus. In contrast to the C and F drainages where the extent of pyrite outcropping was minimal, the extensive pyrite outcrops observed in the L drainage at about 3500 m appear to be having little effect on lakes and streams during the summer. This is because the pyrite outcrops were dry: no water was present to catalyze oxidation and transport acidity to the stream and lakes. The amount of jurbanite precipitation downstream on the White Fork indicates that at high flows during spring snow melt acidification must be more intense.

Two mechanisms of hydrologically controlled surface water acidification are occurring in this area. The first and most prominent during the relatively dry summer months is via pyrite oxidation near perennial sources of water. Groundwater seeps are present, but large flows were not observed in the summer of 1992, the last year of approximately 6 years of drought. The large sources of water and acidity in the summer appear to be where the combination of glacial abrasion and melting ice produce acidic springs (cf. Mahood and Gansecki, Appendix IV: "espresso lakes"). The second mechanism is the oxidation of pyrite that must occur during the winter and spring when snow brings water in contact with pyritic materials that are dry during the summer. This accounts for the considerable jurbanite precipitation along the White Fork in drainage L which did not appear to be as strongly affected as drainage F or C during the summer.

Our ability to use these acid-affected watersheds to model the effects of long-term acidification of Sierra Nevada watersheds is limited. The sources of acidity are very localized and dependent on hydrologic conditions. From a geochemical point of view, this system is analogous to acidic mine drainage. Neutralization of acidity occurs downstream mostly by dilution with circumneutral water of lower ionic strength. The point-source acidity has a limited opportunity to react with the soil and other geologic materials in the watersheds downstream. Overall this system is fundamentally different from one which is uniformly affected by acidic deposition. Acidic deposition would interact equally with all the terrestrial components of the watersheds.

However, at the lake and stream level this model hydrochemical system is useful as a model of the effects of acidification on surface waters in granitic terrain. It provides a chemical gradient along which various species of aquatic life may distribute themselves. The chemistry of the neutralization process is not important to this model,

only the composition of the surface waters. Furthermore, there are some similarities between this hydrochemical system and one in which groundwater is an important component neutralizing acidic deposition. For example, streamflow during acidic rain or snowmelt may be 40-90% groundwater. A large proportion of the snowmelt or rain infiltrates and is neutralized, displacing groundwater which emerges in the stream channel. This neutral groundwater is a major control of the acidification of runoff (Bottomley et al., 1984). The difference between this and the Mt. Pinchot area is that in these drainages the neutralization reactions are nearly all occurring in the stream channel and the alkalinity-producing reactions are in tributaries from watersheds completely separate from the acidity source.

These lakes provide a unique opportunity for the AAPP to obtain direct evidence of the effects of acidification on high elevation Sierra Nevada aquatic ecosystems. A continuous range of acidification intensity due to the addition of SO_4 as sulfuric acid is available from less than pH 5 to over pH 7. The chemical response of the surface waters is predictable and representative of the same conditions that would be expected from intense, chronic anthropogenic additions of sulfuric acid to the system.

SUMMARY

The source of acidity in the Mt. Pinchot area is sulfuric acid produced by the oxidation of pyrite found in metamorphic and granitic rocks in the area. Soils, volcanic activity, mineral springs, and acidic deposition can be ruled out as sources of acidity. The pyrite-bearing formations in the Mt. Pinchot area are highly localized and their influence on surface waters is mediated by the hydrologic characteristics of each watershed. From a geochemical point of view, this system is analogous to acidic mine drainage.

Consistent correspondence was found between acid affected or acidic lakes and the spatial distribution of pyrite-rich outcrops. Not all lakes affected by acidity have low pH. Many of the affected lake-watersheds have sufficient neutralization capacity to maintain neutral pH although SO_4 levels are high. The composition of the acidic (pH $<$ 6) and acid-affected (high $[SO_4]$) lakes is controlled in part by the solubility of the minerals jurbanite ($AlOHSO_4$) and amorphous aluminum hydroxide ($Al(OH)_3$ (a)). This has been verified by solution equilibrium calculations and mineralogical analyses of the white precipitate along the margins of acidified lakes and streams.

The hydrology of these lake watersheds has an important influence on the intensity of acidification found in surface waters. Watersheds with rock glaciers

providing both a mechanical weathering force and water had the most intense acidity in the summer. Where water-pyrite contact was limited, acid production was lower. This situation is hypothesized to change during snow melt, when water-pyrite contact would be greater.

An important question arising from these analyses is whether this geochemical system is an appropriate model for the effects of long-term acidification of Sierra Nevada watersheds. Neutralization of acidity occurs downstream mostly by dilution with circumneutral water of lower ionic strength. This provides a chemical gradient along which various species of aquatic life may distribute themselves. The chemistry of the watershed neutralization process is not important to this model, only that the composition of the surface waters is similar to what might result from acidic deposition. As a result, this area appears to provide good model for acidification effects on aquatic ecosystems.

Chapter 4
FAUNAL ASSEMBLAGES IN ACIDIC AND NON-ACIDIC LAKES

INTRODUCTION

The aquatic biota of lakes can show drastic responses to acidification. For example, responses of zooplankton to acidification commonly include a reduction in species diversity and biomass and a shift in the dominant species (Dillon et al. 1979, Yan and Strus 1980, Marmorek 1984, Nilssen et al. 1984, Havens and DeCosta 1985, Malley and Chang 1986, Havens and DeCosta 1987, Brett 1989). The zoobenthos also includes taxa that are sensitive to acidification although most experimental studies have focused on streams (Hall et al. 1980, Burton et al. 1985, Hall and Ide 1987, Ormerod et al. 1987, Hopkins et al. 1989) rather than on lakes (Roff and Kwiatkowski 1977; Okland and Okland 1980, 1986; Singer 1982; Schindler et al. 1985). Aquatic amphibians and fish also show a variety of physiological, behavioral, and demographic responses to increased acid inputs and, in extreme cases, may be eliminated by acid stress (Schofield 1976, Fromm 1980, Frenette and Dodson 1984, Magnuson et al. 1984, Pierce 1985, Clark and LaZerte 1985).

The lakes and streams of the Sierra Nevada of California are among the most poorly buffered waters in the world (Landers et al. 1987). Although it is known that acidic deposition is occurring in the Sierra Nevada, very little was known until recently about the effects of acid inputs on the biota of Sierran lakes and streams (Dozier et al. 1987, Melack et al. 1989, California Air Resources Board 1988). A series of CARB-funded survey and experimental studies, as well as long-term monitoring of sensitive systems, funded by CARB have contributed substantially to our knowledge regarding the current status of aquatic ecosystems in the Sierra Nevada, and their potential responses to increased acidification (Melack et al. 1987, 1989; Cooper et al. 1988 a, b; Hopkins et al. 1989; Barmuta et al. 1990; Bradford et al. 1993; Jenkins and Kratz 1991). The results of these survey and monitoring studies have provided us with an assessment of regional aquatic resources in the Sierra Nevada; however, investigations of the relationships of the biotic characteristics of surface waters with acidity have been hampered by the restricted range of pH values recorded for most Sierran lakes and streams. In general, almost no lakes or streams with pH's < 5.8 have been found in the surveys. Furthermore, most experimental studies have been conducted in small aquaria, bags, or channels over short time periods (< 2 mos.), so the extent to which the results

of these studies can be applied to whole lake and stream systems over long periods of time (years) is unclear (Cooper and Barmuta 1993).

The recent discovery of naturally-acidic lakes in the High Sierra has provided scientists with a "natural experiment" for evaluating the effects of acidity on the freshwater biota. In this study we have characterized fish, amphibian, zoobenthos, and zooplankton assemblages in a series of acidic and non-acidic lakes in the Bench Lake/Mt. Pinchot area of the Sierra Nevada, and have examined the relationships between the chemical and biological characteristics of these waters. The results of this study have augmented previous survey results to include more acidic conditions, and allowed us to check for congruency with previous small scale experiments. In addition, comparisons of acidic and non-acidic lakes have provided us with a "window" onto the possible responses of whole lakes to long-term chronic acidification.

METHODS

Synoptic Survey

In the Synoptic Survey the 104 lakes were sampled for water chemistry parameters (pH, EC) and surveyed for presence/absence of aquatic vertebrate populations. For each lake pH and EC were measured in the field as described in Chapter 2, elevation was recorded from topographic maps, and maximum depth was estimated visually from shore. Lakes were searched for fish and amphibians by walking along the shoreline of most or all of each lake (Bradford et al. 1993). Amphibians were captured by hand net if necessary to identify to species. Amphibians were recorded as either tadpoles or "adults" (defined as all metamorphosed individuals, regardless of size)

Detailed Survey

In the Detailed Survey of 33 lakes, samples for water chemistry, zooplankton, macroinvertebrates, and fish were taken, and observations of amphibians were also made. pH and EC were measured in the field, and water samples were taken, transferred on ice to the laboratory, and analyzed for pH, ANC, EC, major ions, and aluminum (see Chapter 2).

Owing to impassible barriers, no fish were originally present in the lakes and streams of the Bench Lake/Mt. Pinchot area. Various species of trout (Family Salmonidae) have been introduced to some of the lakes in this area, and were the only

fish present at the time of this survey. Of the 33 lakes visited, 14 were so shallow and clear that investigators could scan the whole water mass from the shoreline and a small raft to ascertain the presence or absence of fish. As a consequence, nets were not used in these lakes. Visual surveys of young trout in shoreline areas, and inflowing or outlet streams, were also conducted to ascertain the presence or absence of reproduction in a given lake-stream system. Fish populations were surveyed in the remaining 19 lakes by using an experimental gill net, which was 43.5 m long, 1.5 m deep, and consisted of 6 panels with mesh sizes of 2.5, 3.1, 3.7, 4.3, 4.9, 5.5, and 6.2 cm. The net was anchored on shore with the smallest mesh in the shallowest water, and deployed along the bottom at an angle perpendicular to the shoreline. To avoid harming fish, this net was scanned continually and any fish captured were removed at 20 minute intervals. If no fish were captured by nightfall the net was left in place over night and checked the following morning. Visual scans of amphibians were conducted from the raft and shoreline areas, and the presence and identity of tadpoles or adults were noted.

Macroinvertebrates in the littoral zone of each lake were sampled by sweeping shallow areas next to the shore with a D net (mesh size = 1 mm) over a 30 minute period. Occasionally, sampling was done over shorter time periods when macroinvertebrates were extremely abundant. D net sweeps followed bottom contours and captured epibenthic and water column invertebrates, as well as surficial sediments. An effort was made to sample all habitats that could be reached from shore. Macroinvertebrates were sorted from debris and sediments in the field, then preserved in 70% ethanol. Macroinvertebrates were identified at 12 to 25X under a dissecting microscope using the keys in Merritt and Cummins (1984).

Zooplankton were sampled from a rubber raft by taking vertical tows with a plankton net (29.5 cm diameter, 40 μm mesh) from the deepest part of each lake. The net was repeatedly lowered to the bottom, then retrieved until substantial numbers of zooplankton were present in samples. Filtered volumes for zooplankton samples were calculated assuming a net efficiency of 50%. Zooplankton samples were preserved in 5% formalin. In the laboratory, zooplankton samples were rinsed on a 45 μm sieve, then washed and diluted with water in a beaker. One milliliter subsamples were removed from the diluted sample with a wide-bore pipette, and subsamples of zooplankton were identified and counted in a Sedgewick-Rafter cell at 40X under a compound microscope. Depending on the abundance of zooplankton, from 1% to entire samples were counted. Microcrustaceans were identified using Edmondson (1959) and rotifers were identified using Stemberger (1979).

RESULTS

Synoptic Survey

Trout. Trout were found in 18 of the 104 lakes surveyed in the Synoptic Survey (fish were observed in 17 and conversations with fishermen indicated that trout were probably present in an additional lake [B-2, Appendix II]). Although it was not always possible to ascertain the identity of fish, golden trout (Oncorhynchus aguabonita), brook trout (Salvelinus fontinalis), and rainbow trout (Oncorhynchus mykiss) were observed in lakes. Trout were absent from all ten lakes with pH's < 6, but were also absent from 76 of the 94 lakes with pH's ≥ 6 (Fisher exact test on trout presence vs. absence in acidic vs. non-acidic lakes, $P = 0.20$; Fig. 4.1; Appendix II). Conductivities were similar in lakes with and without trout (mean in fish lakes = 21.8 μS/cm, SD = 11.5; mean in lakes without fish = 20.2 μS/cm, SD = 18.3), but lakes containing trout tended to be deeper than those lacking trout (mean maximum depth [Z_{max}] = 5.1 m, SD = 3.6 for fish lakes, mean Z_{max} = 3.0 m, SD = 2.5 for lakes lacking fish) (Figs. 4.2, 4.3). Trout were not found in lakes above 3515 m elevation (Fig. 4.4)

Amphibians. The only amphibians observed in lakes were the tadpoles and adults (i.e., metamorphosed individuals of all sizes) of the mountain yellow-legged frog (Rana muscosa) and the tadpoles of the Pacific chorus frog (Pseudacris [=Hyla] regilla) (Appendix II). Tadpoles of the yellow-legged frog were found in 22 lakes (many with adults), and adults alone were found in 14 additional lakes. In general, adults were found over a wider range of conditions than tadpoles. Tadpoles largely did not occur where fish were present. Tadpoles were found in only one of 18 trout lakes, and 21 of 76 non-acidic (pH ≥ 6) lakes lacking trout (chi-square = 4.0, $P = 0.047$). Adults were less affected by the presence of fish (present in 4 of 18 trout lakes and 25 of 76 non-acidic, troutless lakes (chi-square = 0.78, $P = 0.38$).

Yellow-legged frog tadpoles were not observed in any of the 10 acidic lakes (pH < 6; Fig. 4.1), but were seen in 21 of the 76 lakes with pH's ≥ 6 that lacked fish (chi-square = 3.6, $P = 0.056$). In contrast, adult yellow-legged frogs were found in both acidic lakes (4 of 10) and non-acidic, fishless lakes (25 of 76) (chi-square = 0.2, $P = 0.66$). Adults and tadpoles were generally found throughout the range of specific conductances (2 - 102 μs/cm) recorded for the study lakes, and nearly throughout the range of elevation (3120 - 3600 m) (Figs. 4.2, 4.4). Adult frogs were found throughout the range of depths recorded for study lakes (ca. 0.5 - >10 m), but yellow-legged frog tadpoles were found only in lakes having maximum depths of 1.3 to 8 m (Fig. 4.3).

The absence of tadpoles in deep lakes (> 10 m) may be attributed to the presence of trout in many of these lakes. Among non-acidic lakes without fish, yellow-legged frog adults were found alone in shallower lakes than those occupied by yellow-legged frog tadpoles (mean Z_{max} for lakes occupied by adults alone = 1.1 m, SD = 0.4; mean Z_{max} for lakes occupied by tadpoles or tadpoles plus adults = 3.3 m, SD = 1.2).

Pacific chorus frog tadpoles were collected from 6 non-acidic lakes lacking fish, and from one acidic lake (pH = 5.96). Chorus frog tadpoles were the only amphibian in 5 lakes, but occurred with yellow-legged frog tadpoles and adults in one lake, and with only yellow-legged frog adults in the acidic lake. Lakes occupied by chorus frog tadpoles were shallower than those not occupied by chorus frogs (mean Z_{max} = 1.5 m, SD = 1.0 for hylid lakes; mean Z_{max} = 3.45 m, SD = 2.8 for the others), and shallower than lakes occupied by yellow-legged frog adults (mean Z_{max} = 3.2 m, SD = 2.5) and tadpoles (mean Z_{max} = 3.5 m, SD = 1.6). Chorus frog tadpoles were also observed in small, shallow ponds located near the study lakes. Chorus frog tadpoles were observed in lakes with a wide range of conductivities (4 - 40 μS/cm) and elevations (3230 - 3415 m).

Detailed Survey

Trout. Among the 33 lakes included in the detailed survey, trout were observed or collected from seven (Appendix V). Rainbow trout alone were recorded in two lakes, brook trout alone in two lakes, golden trout alone in one lake, rainbow and brook trout together in one lake, and rainbow and brown trout (Salmo trutta) together in one lake (Table 4.1). Trout were found within a relatively narrow range in lake pH, 6.9 to 7.5 (Fig. 4.5). In general, the mean pH of lakes lacking trout was lower, and conductivities and concentrations of most major ions were higher, than in lakes containing trout (Fig. 4.5, Table 4.2). These relationships, however, may be the result of relationships between lake depth and the presence of trout. Trout tended to be found in the larger, deeper lakes (fish lakes: mean Z_{max} = 8.3 m, SD = 2.4, range = 5 - >10 m; fishless lakes: mean Z_{max} = 4.0 m, SD = 2.6, range = 1 - >10 m).

Amphibians. Yellow-legged frog tadpoles were observed (or presumed to occur based on Synoptic Survey results - see Appendix V) in 12 lakes (10 with adults), and adults alone were observed in an additional 8 lakes (Appendix V). Tadpoles were present in only one of the seven lakes containing fish, but were present in 11 of the 18 fishless lakes with pH's $\geq$ 6 (Likelihood chi-square = 4.8, P = 0.028; Fisher exact

Figure 4.1. Frequency distribution of the pH's in the Synoptic Survey for all lakes studied (bottom), lakes where trout were observed (top), and lakes where yellow-legged frog (Rana) tadpoles and adults were observed (middle).

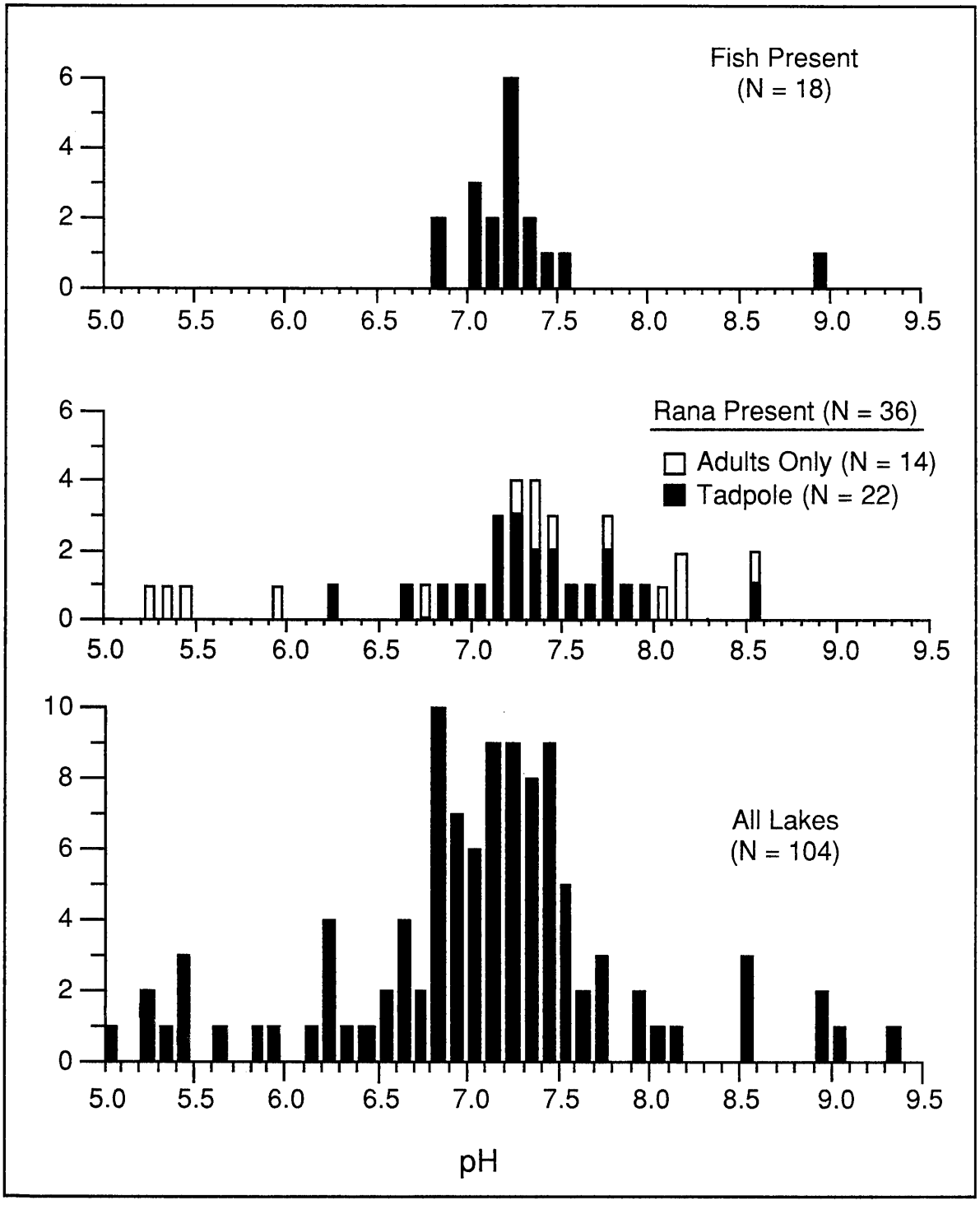

Fish Present
(N = 18)
Rana Present (N = 36)
Adults Only (N = 14)
Tadpole (N = 22)
All Lakes
(N = 104)
pH
5306gr93EAD 1

Figure 4.2. Frequency distribution of the conductivities (μS/cm) in the Synoptic Survey for all lakes studied (bottom), lakes where trout were observed (top), and lakes where yellow-legged frog (Rana) tadpoles and adults were observed (middle). "Uncorrected Specific Conductance" refers to field measurements without correction relative to reference standards. Based on measurement of standards, actual specific conductance = uncorrected specific conductance x 0.9772 - 2.159.

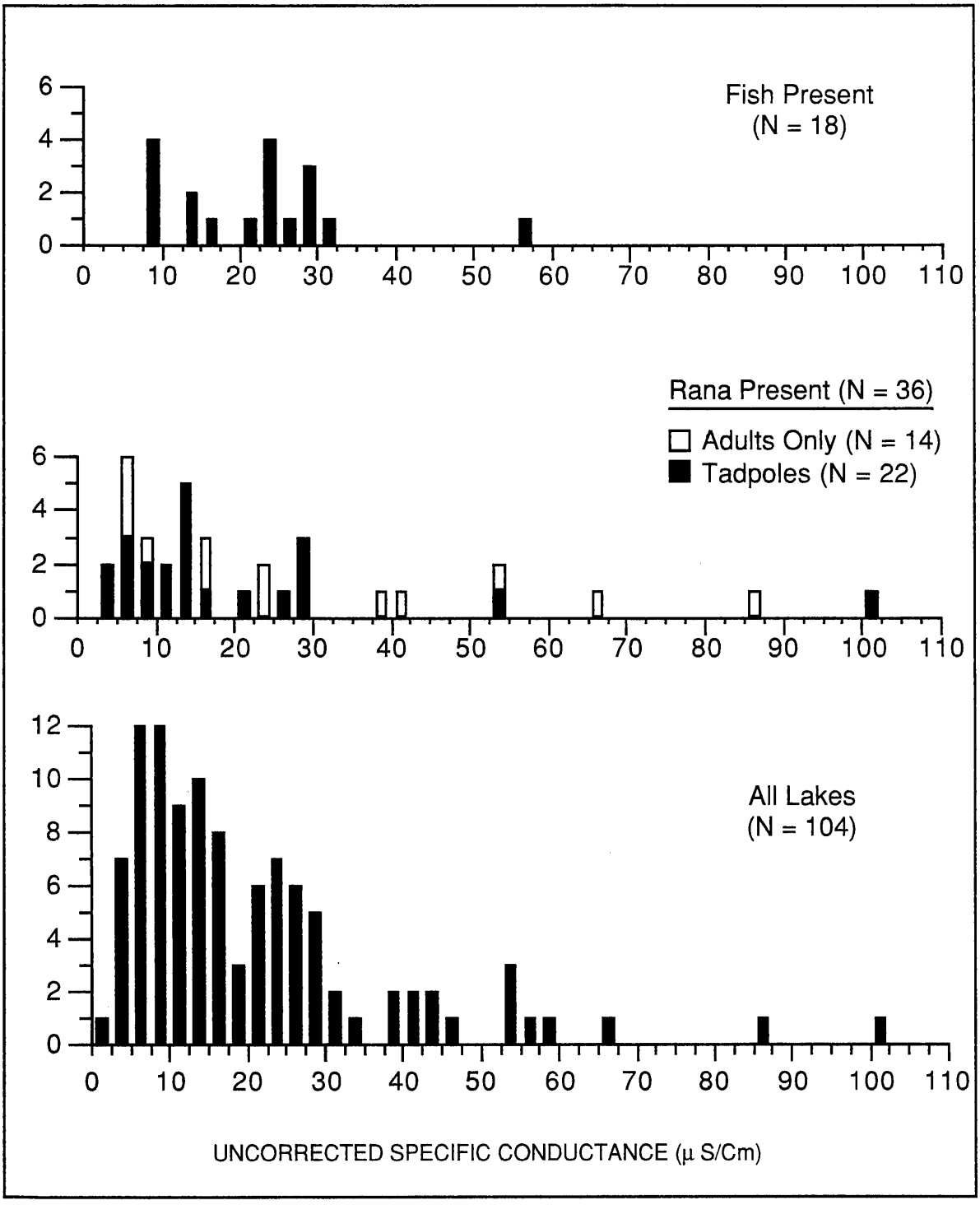

Fish Present
(N = 18)
Rana Present (N = 36)
Adults Only (N = 14)
Tadpoles (N = 22)
All Lakes
(N = 104)
UNCORRECTED SPECIFIC CONDUCTANCE (μ S/Cm)
5306gr93EAD 3

Figure 4.3. Frequency distribution of the maximum depths (Z_{max} in m) in the Synoptic Survey for all lakes studied (bottom), lakes where trout were observed (top), and lakes where yellow-legged frog (Rana) tadpoles and adults were observed (middle).

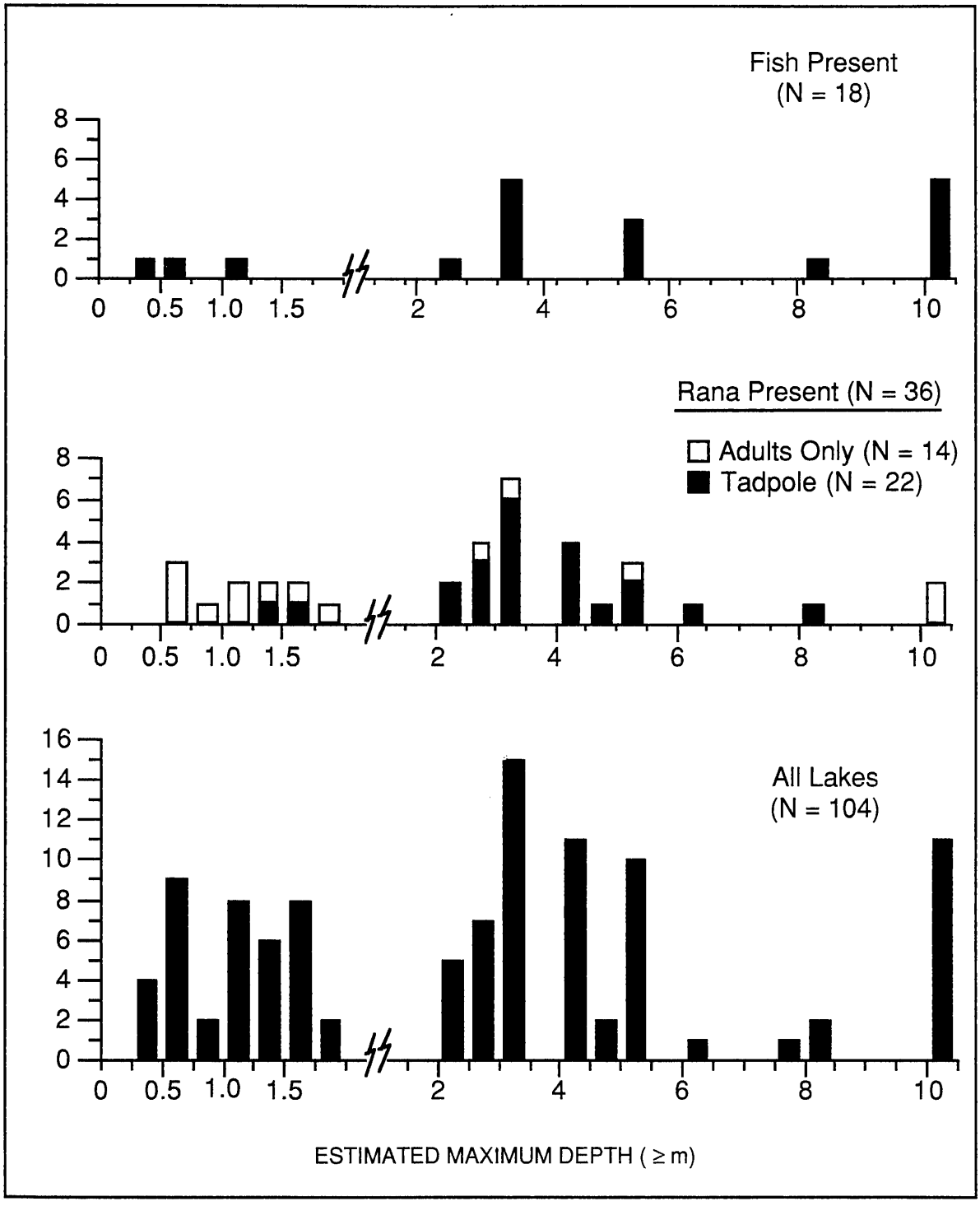
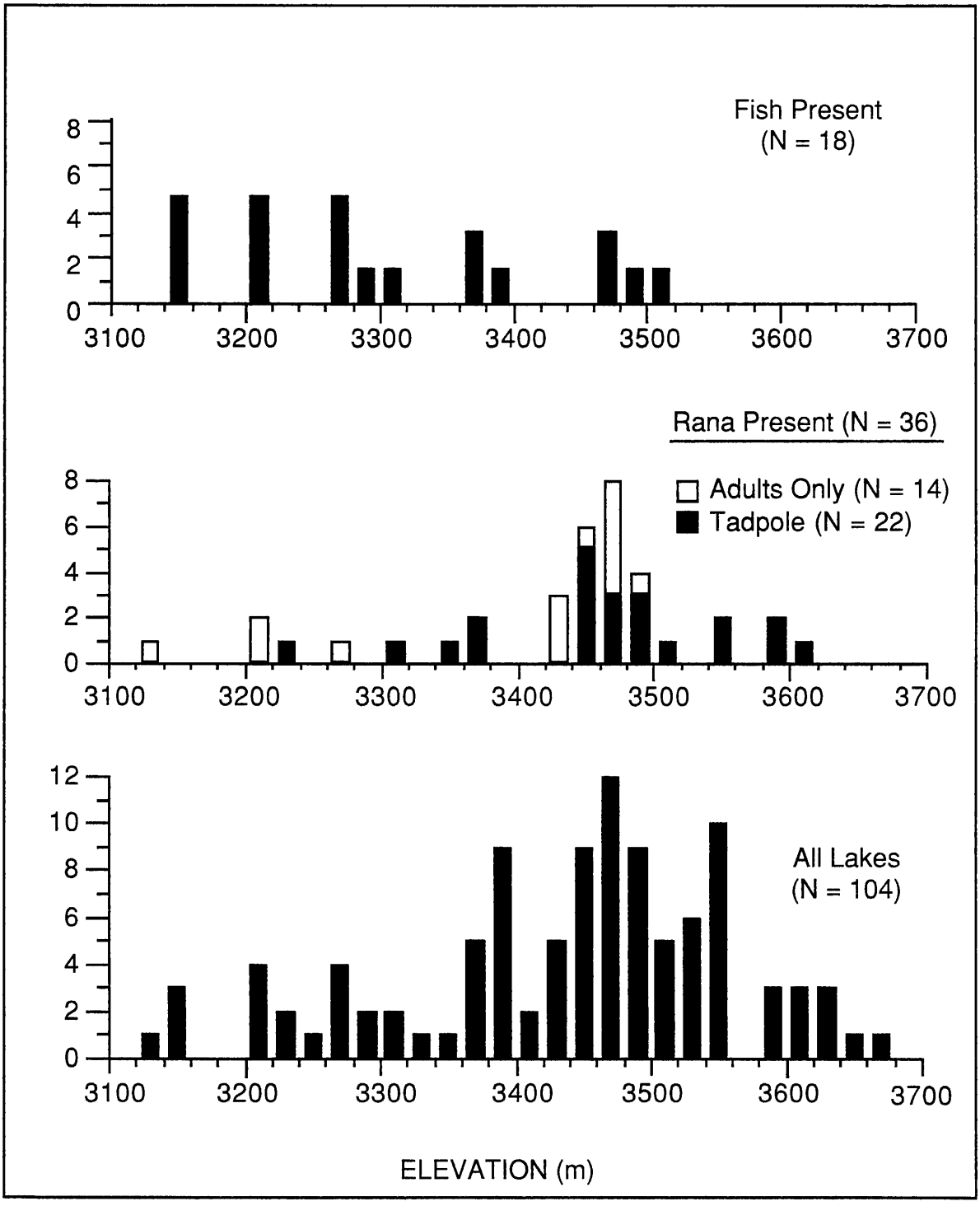
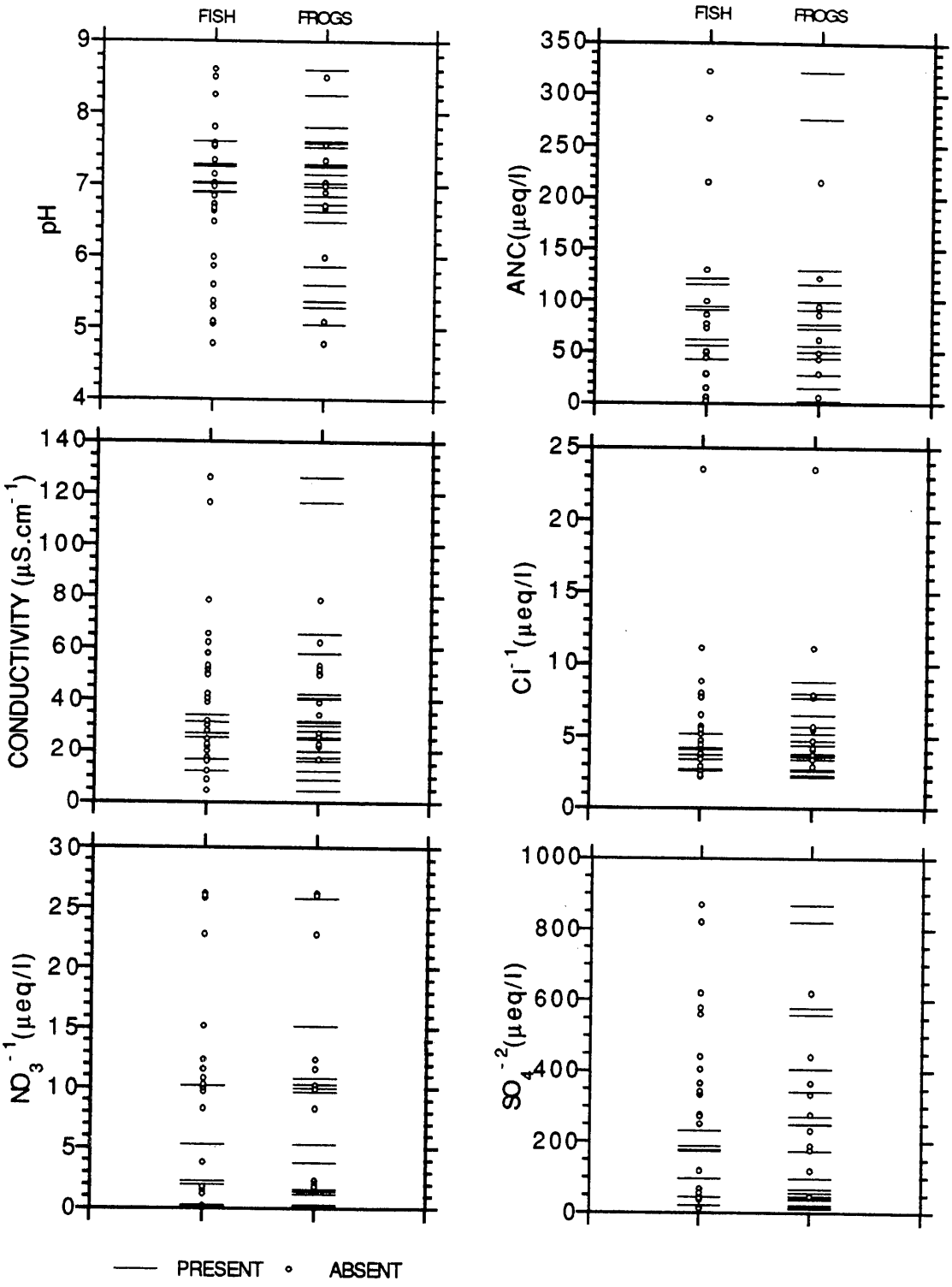

Fish Present
(N = 18)
Rana Present (N = 36)
Adults Only (N = 14)
Tadpole (N = 22)
All Lakes
(N = 104)
ESTIMATED MAXIMUM DEPTH (≥ m)
5306gr93EAD 4

Figure 4.4. Frequency distribution of the elevations (m) in the Synoptic Survey for all lakes studied (bottom), lakes where trout were observed (top), and lakes where yellow-legged frog (Rana) tadpoles and adults were observed (middle).



5306gr93EAD 2

Figure 4.5. pH, ANC (μeq/l), conductivity (μS/cm), Cl^{-1}, NO_3^{-1}, SO_4^{-2}, NH_4^{+1}, Ca^{+2}, Mg^{+2}, Na^{+1}, and K^{+1} values (μeq/l) for lakes in the Detailed Survey containing (---) versus lacking (°) trout (left) and yellow-legged frog adults and/or tadpoles (right) (n = 33 lakes). Lakes having the same value are represented by one point.


FISH
FROGS
pH
ANC(µeq/l)
CONDUCTIVITY (µS.cm⁻¹)
Cl⁻¹(µeq/l)
NO₃⁻¹(µeq/l)
SO₄⁻²(µeq/l)
PRESENT
ABSENT

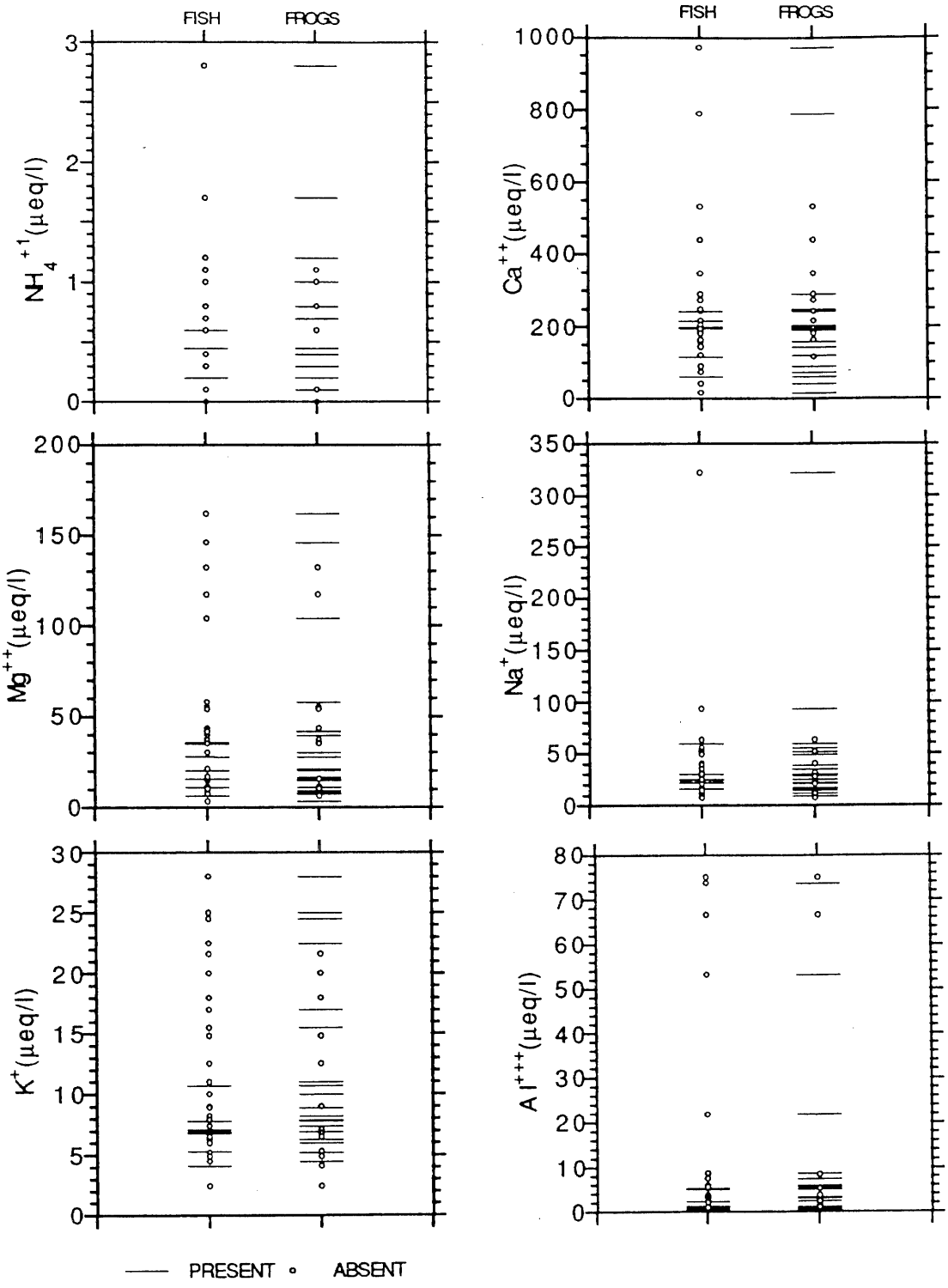

FISH
FROGS
NH_4^{+1}(µeq/l)
Ca^{++}(µeq/l)
Mg^{++}(µeq/l)
Na^{+}(µeq/l)
K^{+}(µeq/l)
Al^{+++}(µeq/l)
PRESENT
ABSENT

Table 4.1. Stocking records and observations for trout in lakes included in Detailed Survey.

Lake ID	Year Stocked[1]	Species Stocked[1,2]	Species Present[1,2]
B-1	1936[3]	O.m.	O.m.
C-4	1936[3]	O.m.	O.m., S.f.
C-5	1969,76,77	O.m.	S.f.[4]
C-21	1936[3]	O.m.	S.f.
C-24	1946,64,71,76,79	O.m.	-
D-4	-[5]	-	O.m.
E-1	1939,46,52,62,67,77	O.m., O.a.[6]	O.m., S.t.
N-3	-	-	O.a.

[1] Stocking records are from Sequoia and Kings Canyon National Parks (NPS) data base, which obtained data largely from California Dept. of Fish and Game (D. Graber, pers. comm.). Observation for species present (1992) are from this study.

[2] Species: O.m. = Oncorhynchus mykiss (rainbow trout), O.a. = Oncorhynchus aquabonita (golden trout), S.f. = Salvelinus fontinalis (brook trout), S.t. = Salmo trutta (brown trout).

[3] Actual date of first planting not known.

[4] Brook trout first observed in 1977 (NPS data base).

[5] No stocking records, but fish have easy access from lakes with fish in E drainage.

[6] O. aquabonita stocked only in 1967.

TABLE 4.2. Summary statistics for the detailed survey of water chemistry relative to vertebrate biota, in 33 lakes in the vicinity of Mt. Pinchot, Kings Canyon National Park, California. Bold/Italic numbers fall outside the 95% confidence intervals for opposing means in the same taxonomic or age group.

	pH	ANC (μeq/l)	EC (μS/cm)	Cl (μeq/l)	NO_3 (μeq/l)	SO_4 (μeq/l)	NH_4 (μM)	Ca (μeq/l)	Mg (μeq/l)	Na (μeq/l)	K (μeq/l)	Al (μeq/l)
FISH PRESENT												
MEAN	***7.15***	83	***24.5***	***3.7***	***3.2***	***134.6***	***0.2***	***174.4***	***21.6***	28.4	***7.0***	***2.4***
MIN	6.90	43	12.3	2.6	0.2	22.7	0.0	59.4	6.4	16.2	4.1	0.7
MAX	7.61	122	34.1	5.2	10.2	232.0	0.6	242.0	35.8	59.5	10.7	5.3
CL(L)	6.95	60	18.7	3.0	0.5	74.7	0.0	126.1	12.9	17.5	5.4	0.9
CL(U)	10.13	153	47.8	8.8	9.9	323.2	3.9	359.7	55.3	91.2	12.4	19.3
n	7	7	7	7	7	7	7	7	7	7	7	7
FISH ABSENT												
MEAN	***6.71***	65	42.7	6.0	8.1	300.8	0.7	259.9	50.7	42.9	***12.9***	15.9
MIN	4.78	-14	4.6	2.2	0.0	12.7	0.0	14.3	3:3	7.2	2.4	0.9
MAX	8.61	322	126.1	23.5	26.2	869.0	2.8	972.0	162.0	322.0	28.0	75.1
CL(L)	6.29	27	31.0	4.3	4.6	198.1	0.4	175.2	32.3	19.3	10.0	5.6
CL(U)	7.13	103	54.4	7.6	11.6	403.4	0.9	344.6	69.1	66.5	15.8	26.2
n	26	23	26	26	26	24	25	26	26	26	26	23
ADULT FROGS PRESENT												
	pH	ANC (μeq/l)	EC (μS/cm)	Cl (μeq/l)	NO_3 (μeq/l)	SO_4 (μeq/l)	NH_4 (μM)	Ca (μeq/l)	Mg (μeq/l)	Na (μeq/l)	K (μeq/l)	Al (μeq/l)
MEAN	6.82	73	39.7	4.8	5.3	271.0	0.6	240.8	47.7	***50.6***	***13.1***	12.1
MIN	5.05	-3	4.6	2.2	0.0	12.7	0.0	14.3	3.3	9.1	4.5	0.7
MAX	8.61	322	126.1	8.8	25.8	869.0	2.8	972.0	162.0	322.0	28.0	73.7
CL(L)	6.33	27	23.8	3.9	1.9	141.3	0.2	124.7	24.8	17.2	9.6	2.3
CL(U)	7.30	118	55.6	5.7	8.6	400.8	0.9	356.9	70.5	84.0	16.7	22.0
n	18	17	18	18	18	18	17	18	18	18	18	17
ADULT FROGS ABSENT												
MEAN	6.79	65	37.9	***6.3***	***9.2***	252.5	0.6	243.0	40.8	26.9	9.8	13.6
MIN	4.78	-14	12.2	2.6	0.0	42.3	0.0	72.8	6.4	7.2	2.4	1.0
MAX	8.50	215	78.4	23.5	26.2	620.0	1.7	530.0	132.0	63.0	21.6	75.1
CL(L)	6.30	29	28.1	3.6	4.5	157.4	0.3	181.3	21.3	19.1	6.7	0.0
CL(U)	7.27	101	47.6	9.0	14.0	347.5	0.8	304.7	60.2	34.6	13.0	27.8
n	15	13	15	15	15	13	15	15	15	15	15	13

TABLE 4.2. Summary statistics for the detailed survey of water chemistry relative to vertebrate biota, in 33 lakes in the vicinity of Mt. Pinchot, Kings Canyon National Park, California. Bold/Italic numbers fall outside the 95% confidence intervals for opposing means in the same taxonomic or age group (concluded).

	TADPOLES PRESENT/FISH ABSENT											
	pH	ANC (μeq/l)	EC (μS/cm)	Cl (μeq/l)	NO_3 (μeq/l)	SO_4 (μeq/l)	NH_4 (μM)	Ca (μeq/l)	Mg (μeq/l)	Na (μeq/l)	K (μeq/l)	Al (μeq/l)
MEAN	***7.28***	***103***	38.0	5.1	***1.9***	***228.0***	***0.9***	256.8	***26.6***	***55.6***	10.7	***3.5***
MIN	6.49	15	4.6	2.2	0.1	12.7	0.0	14.3	3.3	9.1	4.5	0.9
MAX	8.61	322	126.1	8.8	10.0	869.0	2.8	972.0	104.0	322.0	28.0	8.7
CL(L)	6.86	40	12.4	3.7	0.1	36.5	0.3	65.4	9.1	0.5	6.4	2.1
CL(U)	7.69	165	63.6	6.5	3.6	419.5	1.4	448.2	44.0	110.7	15.1	5.0
n	11	11	11	11	11	11	10	11	11	11	11	11
	TADPOLES ABSENT/FISH ABSENT											
MEAN	***6.29***	***30***	46.2	***6.6***	***12.7***	362.3	0.5	262.2	***68.4***	33.5	14.4	***27.3***
MIN	4.78	-14	21.8	2.3	0.0	48.0	0.0	142.0	10.3	7.2	2.4	1.0
MAX	8.50	215	78.4	23.5	26.2	620.0	1.1	530.0	162.0	63.0	25.0	75.1
CL(L)	5.71	-7	37.7	4.0	8.1	269.1	0.3	207.2	42.4	24.6	10.6	9.7
CL(U)	6.88	68	54.6	9.3	17.4	455.6	0.7	317.2	94.3	42.4	18.2	44.8
n	15	12	15	15	15	13	15	15	15	15	15	12

test, P = 0.07). In the single lake containing both fish and tadpoles (lake N-3), tadpoles were found only in an extensive shallow rocky area. In contrast to tadpoles, adult frogs were seen in 3 of the seven fish lakes, and 10 of the 18 fishless lakes with pH's $\geq$ 6 (Likelihood chi-square = 0.33, P = 0.57; Fisher exact test, P = 0.67). No individuals of the Pacific chorus frog were found in lakes in the Detailed Survey, although they occurred in some ponds near these lakes.

Yellow-legged frog tadpoles were not observed in any of the 8 acidic lakes (all lacked fish), but occurred in 11 of 18 non-acidic lakes lacking fish (Likelihood chi-square = 11.4, P = 0.001; Fisher exact test, P = 0.007). In contrast, adults were seen in lakes with pH's as low as 5.0, occurring in 5 of 8 acidic lakes and 10 of 18 non-acidic lakes lacking fish (Likelihood chi-square = 0.11, P = 0.74; Fisher exact test, P = 1.0) (Fig. 4.5). This difference between the distributions of tadpoles and adults relative to pH was conspicuous in areas containing both acidic and non-acidic lakes in close proximity. For example, both acidic Lake F-14 and nearby acidic Lake F-13N contained only adult frogs, whereas non-acidic Lake F-11, which was located 0.1 km downstream from Lake F-13N, contained both adults and tadpoles. Similarly, non-acidic Lake F-13S was separated from acidic Lake F-13N by a narrow causeway (ca. 25 m wide); both contained adults, but only the non-acidic lake contained tadpoles.

Lakes containing either adults or tadpoles were recorded from the range of ANCs, conductivities and major ion concentrations found for all study lakes (Table 4.2). However, when fishless lakes containing versus lacking tadpoles are compared, strong differences in water chemistry are apparent (Table 4.2). In general the mean pH of lakes lacking tadpoles was lower, and concentrations of most major ions were higher, than in lakes containing tadpoles (Table 4.2).

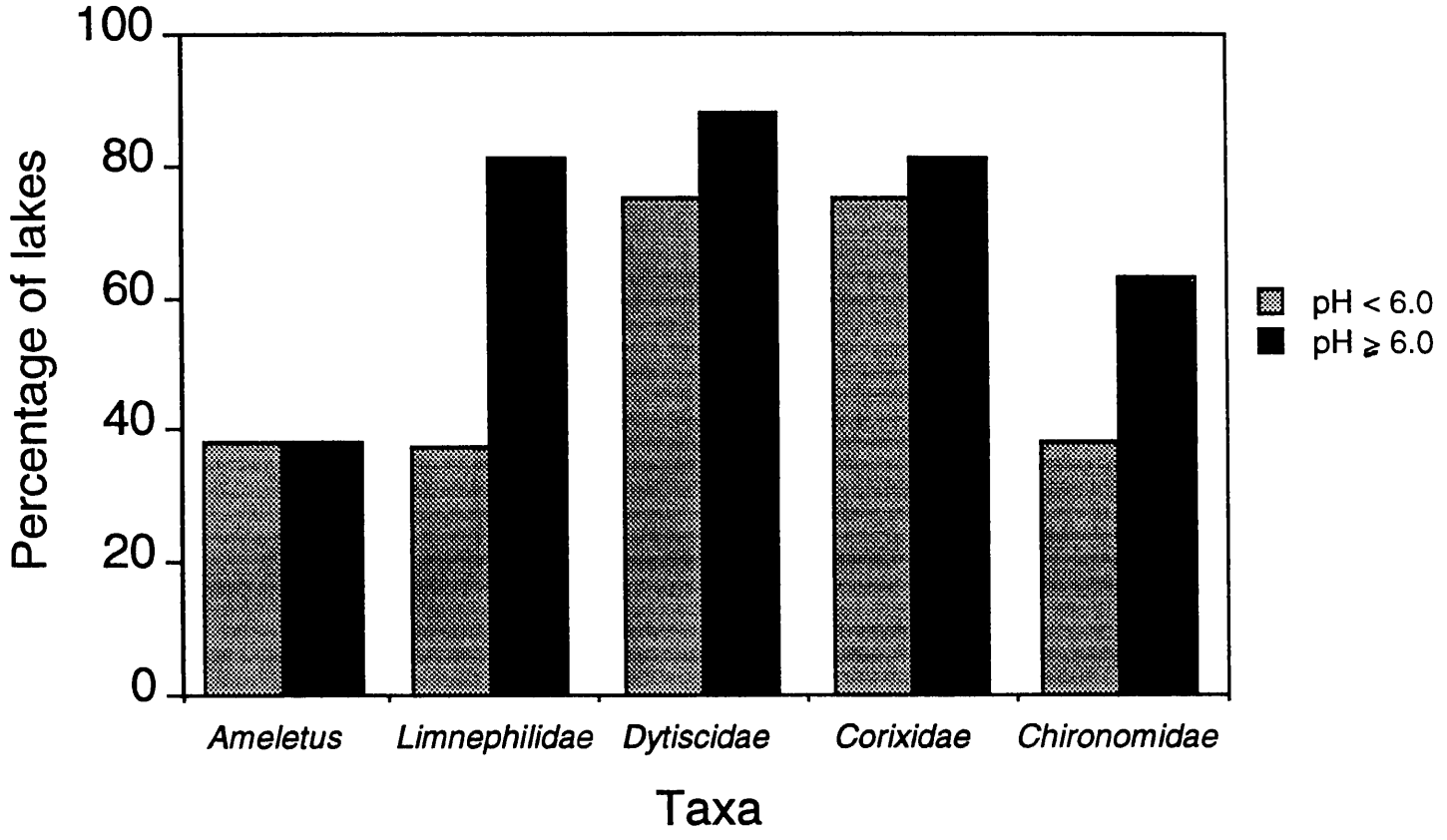
Macroinvertebrates. A variety of macroinvertebrate taxa were collected from the littoral zones of the study lakes, including the larvae of mayflies (Baetidae: Baetis, Callibaetis; Siphlonuridae: Ameletus; Heptageniidae: Cinygmula), stoneflies (Perlodidae: Isoperla), caddisflies (Polycentropodidae: Polycentropus variegatus; Limnephilidae: Desmona bethula, Ecclisomyia, Hesperophylax), damselfies (Coenagrionidae: Enallagma), and true flies (Dixidae: Dixa; Culicidae: Culex; Chironomidae: Chironomini, Orthocladiinae, Tanypodinae, Tanytarsini); larvae and adults of true bugs (Notonectidae: Notonecta; Corixidae: Graptocorixa, Hesperocorixa, Sigara; Gerridae: Gerris) and dytiscid beetles (Dytiscidae: Agabus, Deronectes, Hydaticus modesto, Hydroporus, Hydrovatus, Rhantus; Gyrinidae: Gyrinus punctellus); and all life history stages of water mites (Acarina), sphaerid clams (Pisidium), and

amphipods (Hyallela azteca) (Appendix VI). Of the macroinvertebrate taxa, only the limnephilid caddis larvae seemed to show any relationship with pH, being found in only 37% of the acidic lakes but 81 % of the nonacidic lakes lacking fish (Fisher's exact test, P = 0.065; Fig. 4.6). Within this family, Hesperophylax was not collected from acidic lakes but was collected from half of the non-acidic lakes without fish (Fisher's exact test, P = 0.022), whereas Desmona was present in both acidic and non-acidic lakes (Fisher's exact test, P = 0.66) (Fig. 4.7). Most other common taxa, including mayflies in general, Ameletus, Dytiscidae, Corixidae, and Chironomidae, were collected in simlar frequencies in acidic and non-acidic lakes (Figs. 4.6, 4.7). Among rare taxa, baetid and heptageniid mayflies, Sialis latreille, Notonecta, sphaerid clams, and amphipods were not collected from acidic lakes, but were collected from a small number of non-acidic lakes (Fig. 4.7, Appendix VI).

Most common macroinvertebrate taxa showed relationships with the presence or absence of fish. Limnephilid caddis larvae, mayfly nymphs, dytiscid beetles, and corixids were rare or absent in fish lakes, but were commonly collected in non-acidic lakes lacking fish (Fisher exact tests for these four groups, P's = 0.001 to 0.026; Fig. 4.6). Chironomids were collected from lakes containing and lacking fish. Among rare taxa, Notonecta was only collected in lakes lacking fish, the caddis larvae Polycentropus variegatus and Ecclisomyia were only collected in lakes containing fish, and Sialis latreille, acarids, and Pisidium were collected from both fish and fishless lakes (Appendix VI).

Zooplankton. Zooplankton taxa frequently collected in the surveyed lakes included diaptomid copepods (Diaptomus eiseni, D. shoshone, D. signicauda), cladocerans (Daphnidae: Daphnia rosea, D. middendorffiana; Chydoridae: Chydorus sphaericus), and rotifers (Lecane spp., Trichotria tetractis, Lepadella spp., Polyarthra sp., Keratella cochlearis). Taxa occasionally collected included the cladocerans Holopedium gibberum, Bosmina longirostris, Macrothrix hirsuticornis, Polyphemus pediculus, Scapholebris kingii, Eurycercus lamellatus, and Alona sp., and the rotifers Hexarthra mira, Trichocerca capucina, Collotheca mutabilis, Conochilus unicornis, Keratella taurocephala, Monostyla lunaris, and Notholca labis (Appendix VII). Because Diaptomus eiseni and D. shoshone are similar in size and habitat, and never co-occurred, these taxa were combined as "large Diaptomus" for statistical analyses. The two Daphnia species and the two Keratella species also were considered together for some statistical analyses. There were insufficient data for rare taxa to conduct statistical analyses, and analyses were not performed on littoral taxa (Lecane, Lepadella)

Figure 4.6. Top: Among fishless lakes, the percentages of acidic (pH $<$ 6.0; left) and non-acidic (pH $\geq$ 6.0; right) lakes containing designated macroinvertebrate taxa. Eight acidic and 16 non-acidic lakes lacking fish were sampled. Bottom: Among non-acidic lakes, the percentages of lakes containing (left) and lacking (right) fish which contained designated taxa. Seven non-acidic lakes contained fish and 16 non-acidic lakes lacked fish.


100
80
60
40
20
0
Percentage of lakes
pH < 6.0
pH ≥ 6.0
Ameletus
Limnephilidae
Dytiscidae
Corixidae
Chironomidae
Taxa

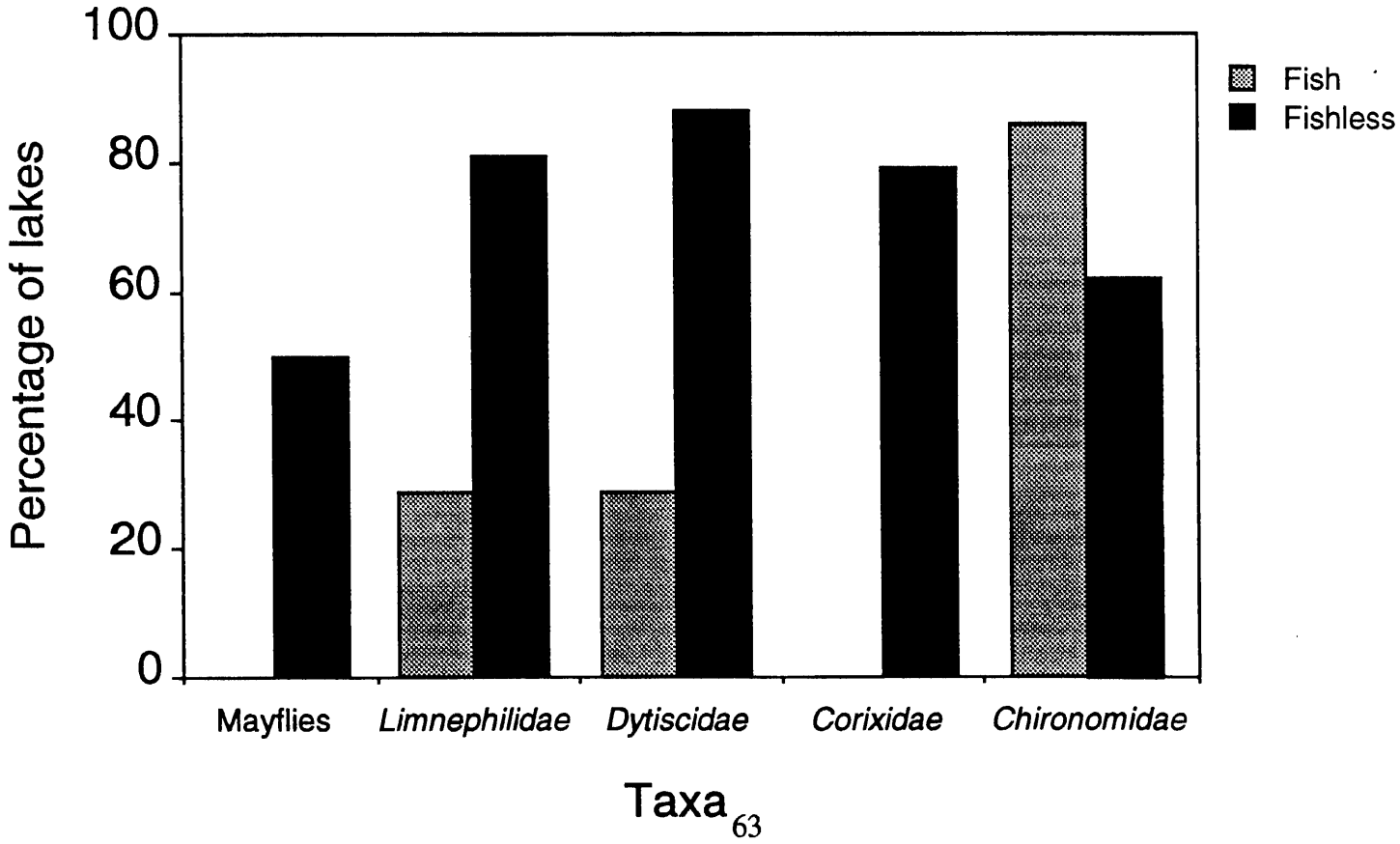
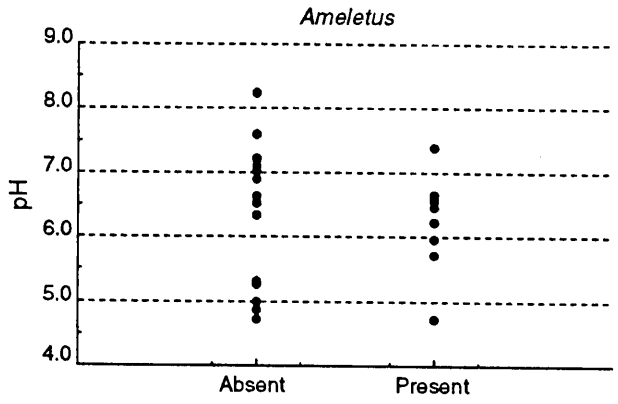
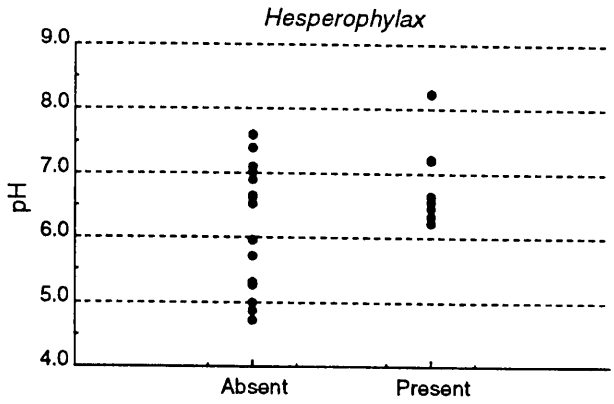
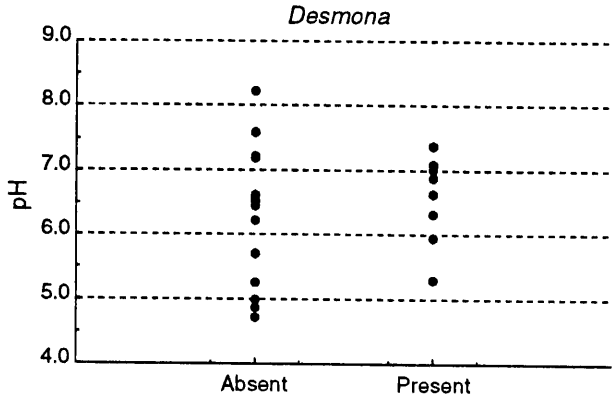
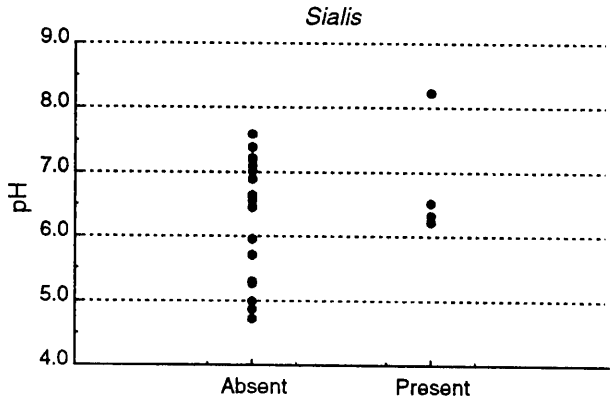

100
80
60
40
20
0
Percentage of lakes
Fish
Fishless
Mayflies
Limnephilidae
Dytiscidae
Corixidae
Chironomidae
Taxa

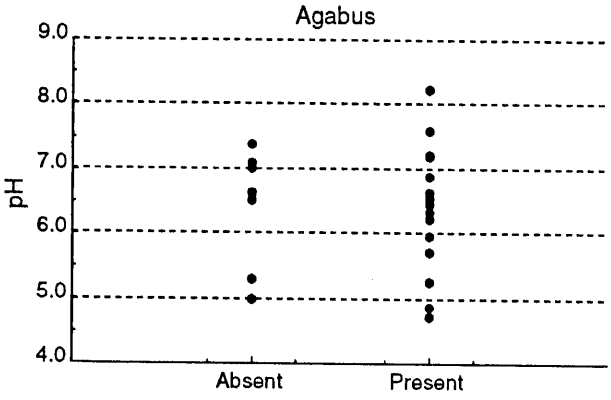
Figure 4.7. pH values for fishless lakes from which given macroinvertebrate taxa were collected ("Present") or were not collected ("Absent") in the Detailed Survey (n = 24 lakes). Lakes having the same value are represented by one point.

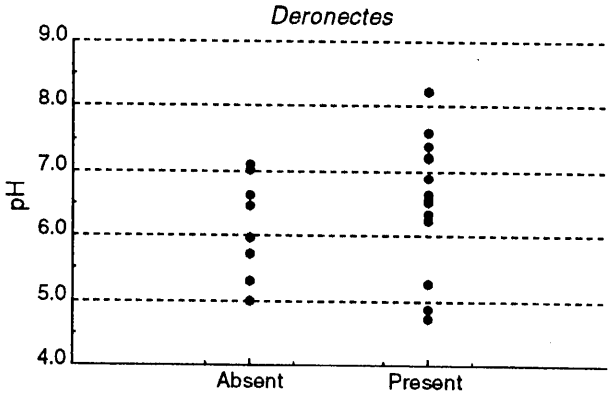

Ameletus
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present

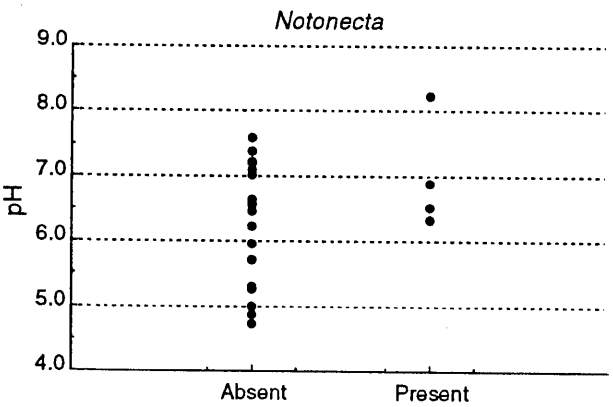

Hesperophylax
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present

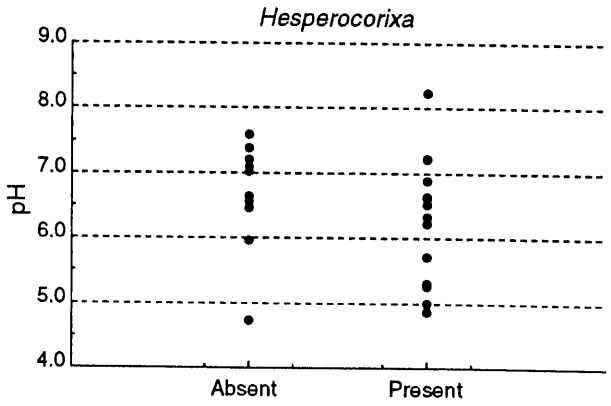

Desmona
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present


Sialis
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present


Agabus
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present


Deronectes
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present


Notonecta
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present


Hesperocorixa
9.0
8.0
7.0
6.0
5.0
4.0
pH
Absent
Present

because these probably represented contaminants from bottom sediments. Analyses of taxon-specific data, then, were restricted to commonly collected planktonic taxa. All taxa were considered, however, when examining relationships between species richness and pH.

The largest-bodied zooplankton taxa, i.e. Diaptomus eiseni/shoshone and Daphnia middendorffiana, were rare or absent in fish lakes (14 and 0% of lakes, respectively), but were commonly collected in non-acidic lakes lacking fish (72 and 55% of lakes) (Fisher exact tests, P's = 0.02) (Fig. 4.8). Daphnia rosea and Keratella spp. tended to be collected more commonly in fish than non-acidic fishless lakes; however, these patterns were not significant (Fisher exact tests, P's = 0.30 - 0.63; Fig. 4.8). Diaptomus signicauda, Chydorus sphaericus, and Polyarthra sp. were collected with similar frequencies from fish and fishless lakes. Almost all rare taxa were collected in both lakes containing and lacking fish.

In acid lakes (pH < 6.0) lacking fish, Diaptomus eiseni/shoshone and Diaptomus signicauda were rarely collected (12 - 25 %), and Daphnia spp. were absent, but these microcrustaceans were frequently collected from non-acidic lakes lacking fish (72-94% of lakes) (Fisher exact tests, P's = 0.001 to 0.009) (Figs. 4.9, 4.10). Although regressions of the log-transformed abundances of these taxa against pH for fishless lakes were significant, there was a lot of scatter in the data at higher pH's, and coefficients of determination were often low (r^2s = 0.21 to 0.35; Fig. 4.11). Polyarthra sp. also tended to be collected more frequently in non-acidic than acidic lakes (25% of acidic fishless lakes, 70% of non-acidic fishless lakes; Fisher's exact test, P = 0.08). Other common zooplankton taxa, including the cladoceran Chydorus sphaericus and the rotifers Trichotria tetractis and Keratella cochlearis/taurocephala were collected at similar frequencies in acidic and non-acidic, fishless lakes (Figs. 4.9, 4.10). Among rarer or littoral species, Macrothrix, Alona, Lecane, Trichocerca, and Conochilus were absent from acidic lakes, but were present in small numbers of non-acidic lakes (3 to 10 lakes depending on the species) (Appendix VII). Lepadella and Collotheca were collected from both acidic and non-acidic lakes. Microcrustacean species richness increased significantly with increasing pH in fishless lakes, while rotifer species richness did not (Fig. 4.12).

DISCUSSION

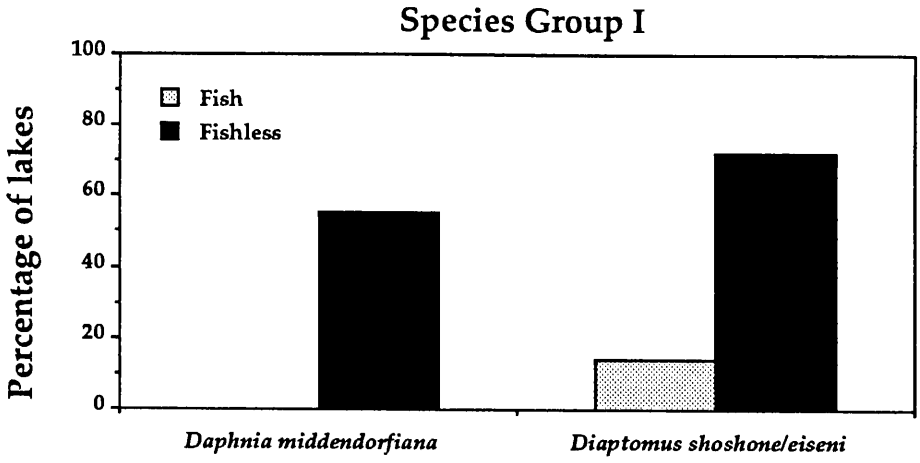
Trout

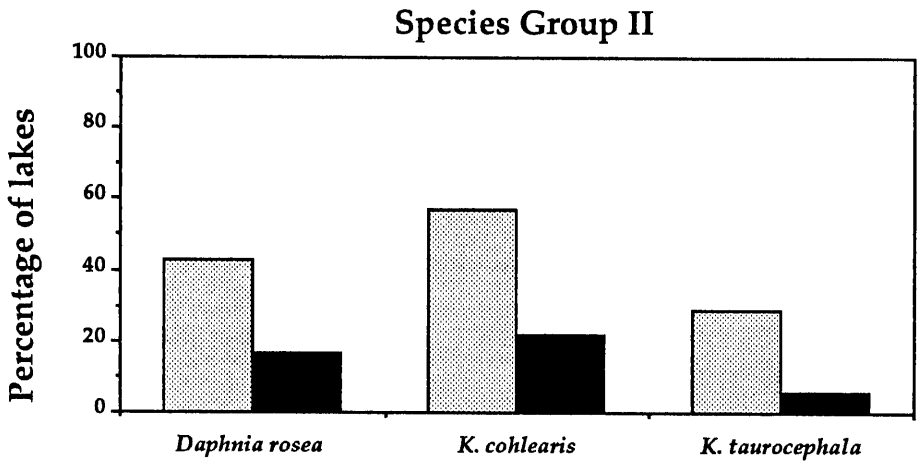
Trout were originally absent from many waters of the High Sierra, including lakes in the Bench Lake/Mt. Pinchot area, but have been widely stocked in Sierran lakes by packers, anglers, and the California Fish and Game Commission (Christenson 1977). To determine if some of the patterns in fish distributions that we observed were owing to patterns in fish stocking by governmental agencies, we examined the stocking records of the California Department of Fish and Game, Bishop office, and the National Park database dealing with fish in Kings Canyon National Park (courtesy of Dr. D. Graber). For the watersheds represented in the Detailed Survey (i.e., B, C, D, E, F, L, N, O, P), there are no stocking records for fish in the F, L, O and P drainages, and fish are currently absent from those basins. There are old stocking records and observations of trout in the B, C, D, and E drainages and we observed fish in large, deep lakes in these basins. Lakes in these drainages that lack fish are very shallow, and prone to complete freezing or winterkill conditions, or are physically isolated from the main stream systems. Lake N-3 is anomalous in that it contains trout, yet it has no stocking records. However, this lake is located near the John Muir Trial and several waters containing trout.

The only lake that we know was stocked but does not now contain trout is the acidic Lake C-24 (Table 4.1). This lake was planted with rainbow trout at least five times, in 1946, 1964, 1971, 1976, and 1979. Because this lake lacks inflowing and outflowing streams, which would be necessary for rainbow trout spawning, and because rainbow trout are unlikely to live 13 years, the absence of trout from this lake is, perhaps, not surprising. Rainbow trout were observed in this lake in 1964 (NPS data base), but it is not clear if trout were observed before or after fish were stocked in that year. It is also not known if the chemistry of this lake has remained constant for the last 30 years, but this lake has remained acidic throughout the 1980's and early 1990's (Whiting et al. 1989; G.R. Bradford, pers. comm.).

The limited stocking records and survey data contain a few surprises (Table 4.1). For example, lakes in the C drainage were only stocked with rainbow trout, but brook trout were observed in Lake C-5 in 1977 (NPS data base) and had spread to Lakes C-4 and C-21 by the time of this survey. The appearance of brook trout in the C drainage can probably be attributed to unrecorded stocking by packers, anglers, or California Department of Fish and Game personnel. More puzzling is the presence of brown trout

Figure 4.8. Among non-acidic lakes (pH $\geq$ 6.0), the percentages of fish (left) and fishless (right) lakes which contained the designated zooplankton taxa. Seven non-acidic lakes containing fish and 17 (rotifers) or 18 (microcrustaceans) non-acidic lakes lacking fish were sampled. Group I species were more frequently collected in fishless than fish lakes, Group II species tended to show the opposite pattern, and Group III species showed no relationship with fish presence vs. absence.


Species Group I
Percentage of lakes
100
80
60
40
20
0
Fish
Fishless
Daphnia middendorfiana
Diaptomus shoshone/eiseni


Species Group II
Percentage of lakes
100
80
60
40
20
0
Daphnia rosea
K. cohlearis
K. taurocephala

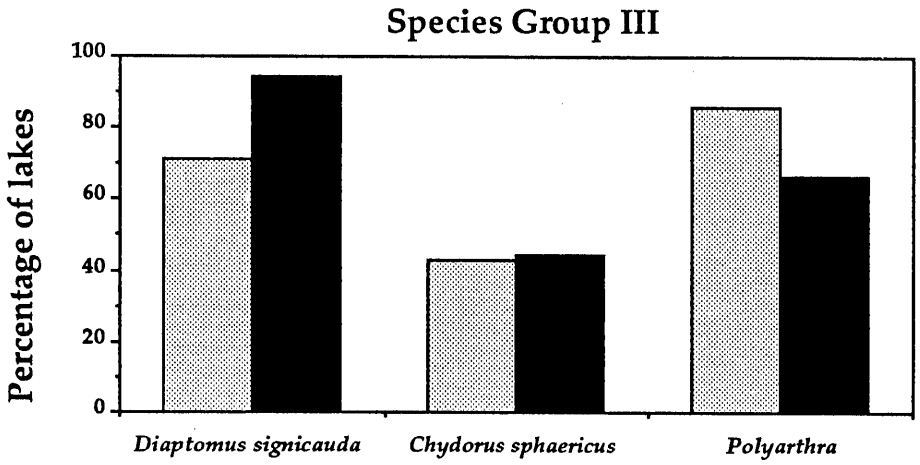
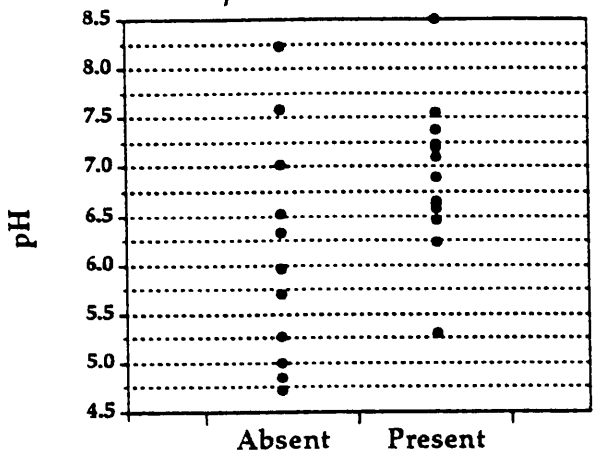
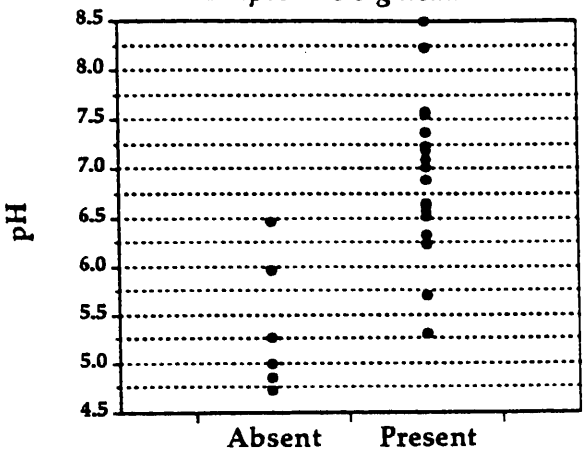

Species Group III
Percentage of lakes
100
80
60
40
20
0
Diaptomus signicauda
Chydorus sphaericus
Polyarthra

Figure 4.9. pH values for fishless lakes from which the designated zooplankton taxa were collected ("Present") or were not collected ("Absent") in the Detailed Survey (n=25 for rotifers, 26 for microcrustaceans).

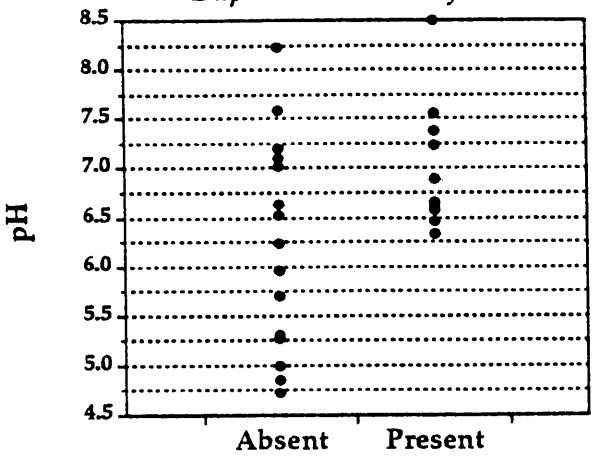
Diaptomus shoshone/eiseni



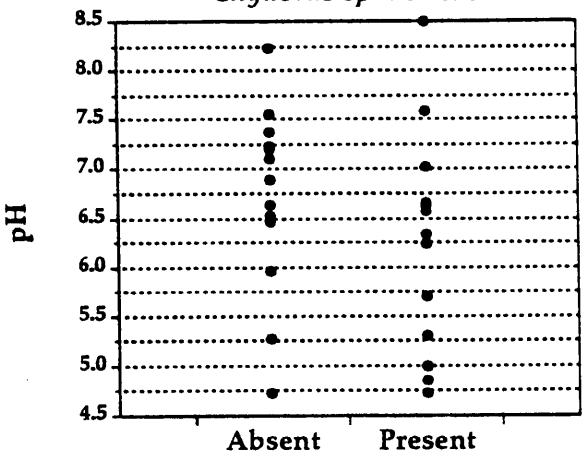
Diaptomus signicauda



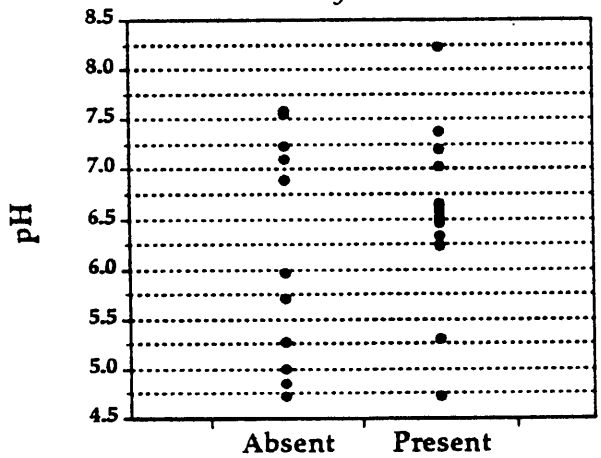
Daphnia middendorfiana



Chydorus sphaericus



Polyarthra



Keratella cochlearis

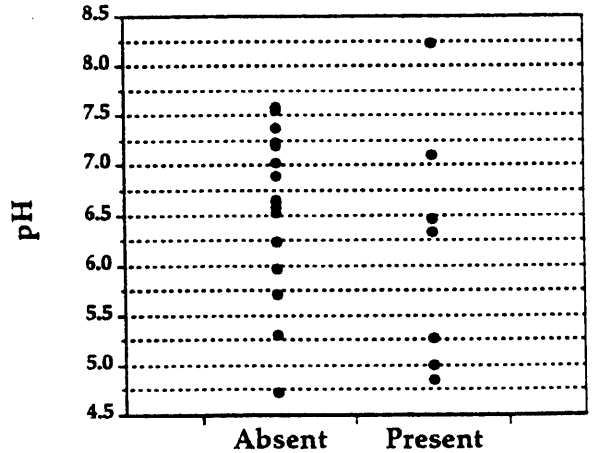
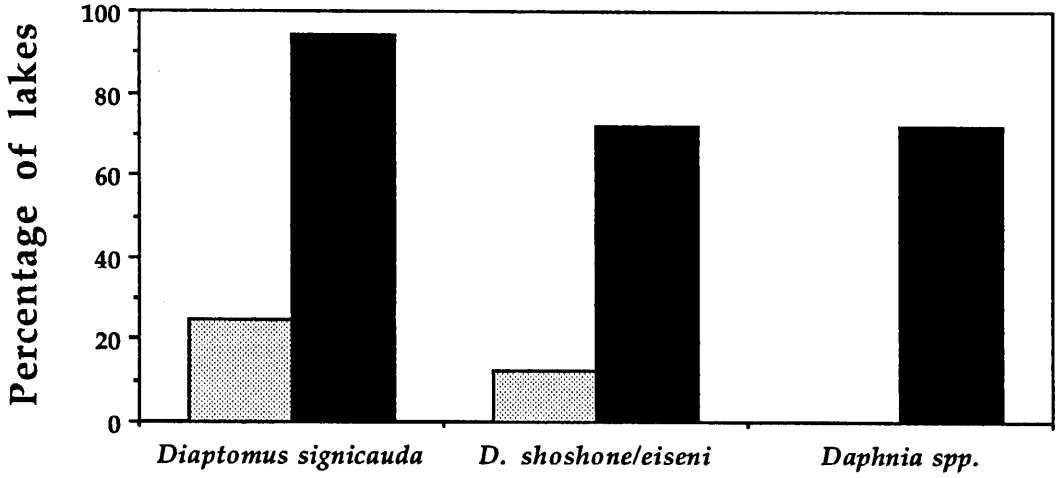


Figure 4.10. Among fishless lakes, the percentages of acidic and non-acidic lakes containing designated zooplankton taxa in the Detailed Survey. Eight acidic and 17 (rotifers) or 18 (microcrustaceans) non-acidic lakes lacking fish were sampled.


Percentage of lakes
100
80
60
40
20
0
Diaptomus signicauda
D. shoshone/eiseni
Daphnia spp.

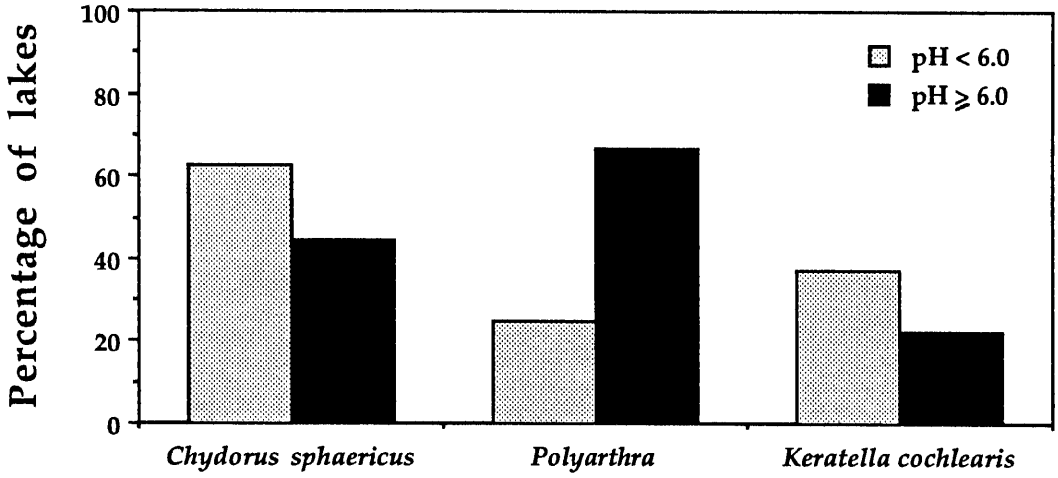
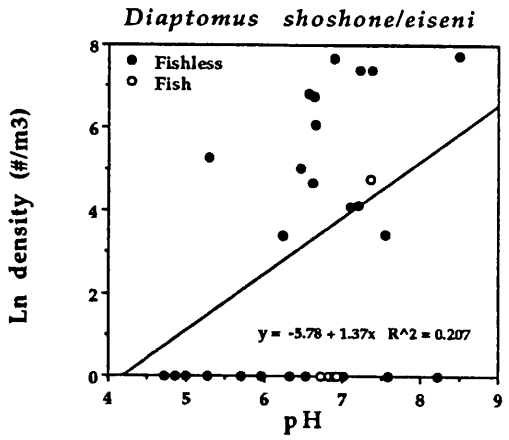
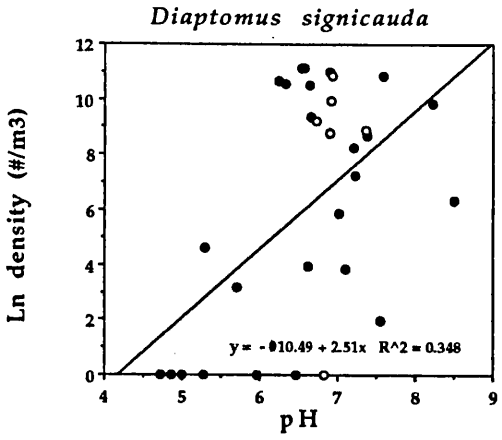
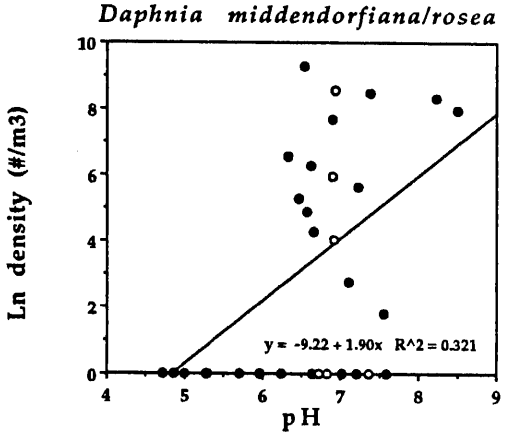
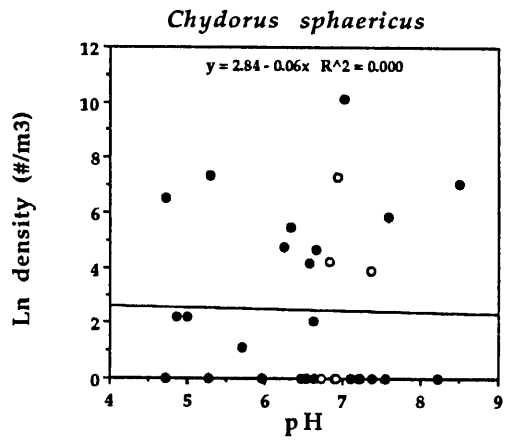

Percentage of lakes
100
80
60
40
20
0
pH < 6.0
pH ≥ 6.0
Chydorus sphaericus
Polyarthra
Keratella cochlearis

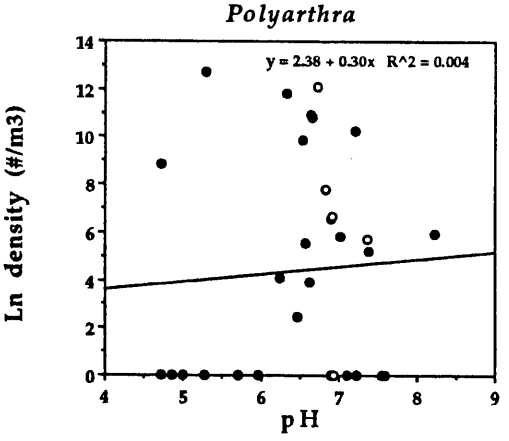
Figure 4.11. Relationships between log-transformed abundances (#/m^3) and pH for common zooplankton taxa for all lakes in the Detailed Survey (n = 33). Regression lines were fitted by the procedure of least squares to data from fishless lakes only (n = 25 for rotifers, 26 for microcrustaceans). Regression equations and coefficients of determination are included.


Diaptomus shoshone/eiseni
Fishless
Fish
y = -5.78 + 1.37x R^2 = 0.207
Ln density (#/m3)
pH


Diaptomus signicauda
y = -10.49 + 2.51x R^2 = 0.348
Ln density (#/m3)
pH


Daphnia middendorfiana/rosea
y = -9.22 + 1.90x R^2 = 0.321
Ln density (#/m3)
pH


Chydorus sphaericus
y = 2.84 - 0.06x R^2 = 0.000
Ln density (#/m3)
pH


Polyarthra
y = 2.38 + 0.30x R^2 = 0.004
Ln density (#/m3)
pH

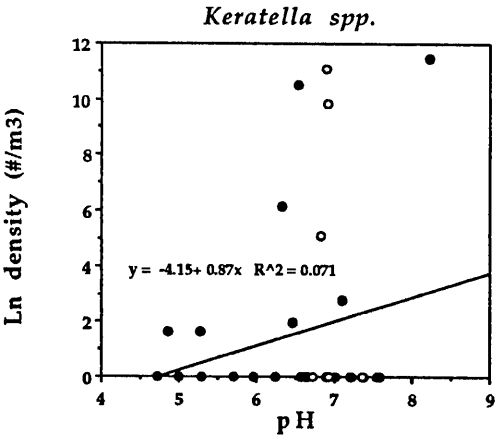
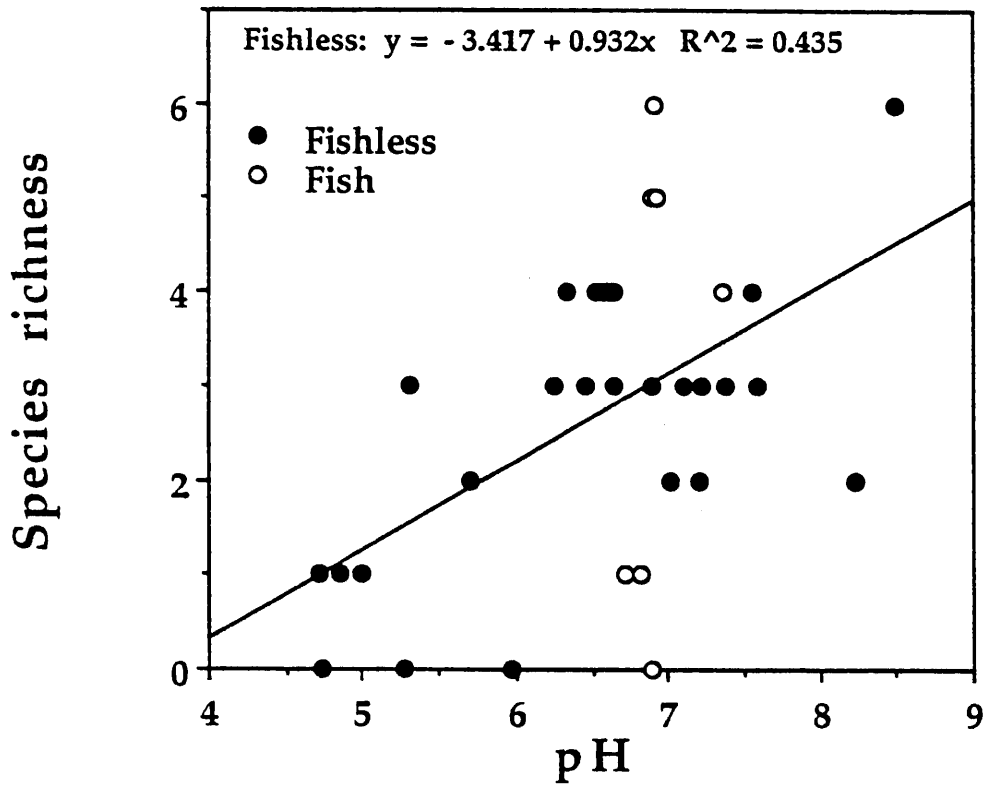
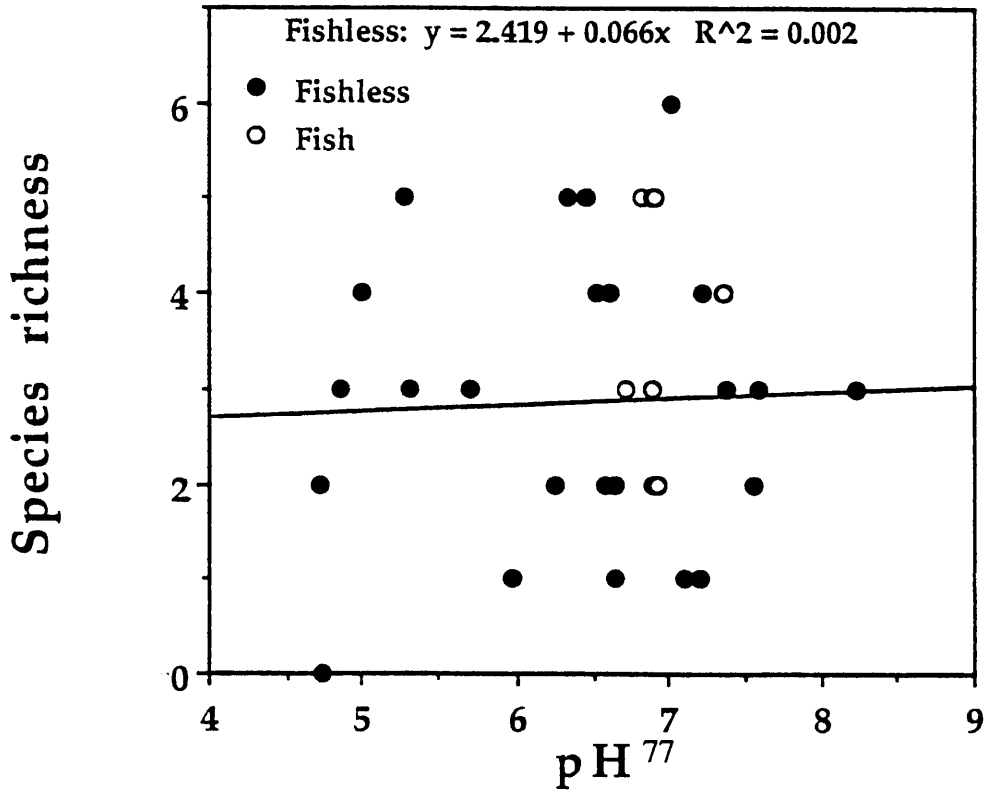

Keratella spp.
y = -4.15+ 0.87x R^2 = 0.071
Ln density (#/m3)
pH

Figure 4.12. Relationships between microcrustacean (top) or rotifer (bottom) species richness and pH for all lakes in the Detailed Survey (n = 33). Regression lines were fitted by the procedure of least squares to data from fishless lakes only (n = 25 for rotifers, 26 for microcrustaceans). Regression equations and coefficients of determination are included.

Crustaceans



Rotifers



in Lake E-1; we have no explanation for the presence of this species in this lake. In general, however, these data suggest that trout were planted in the largest, deepest, and most accessible lakes near the John Muir Trail and, in some cases, spread to other lakes through connecting streams. There was no concerted effort to plant all waters in this area, and most of the acidic lakes (F and L drainages) were so inaccessible that they were probably never planted. Although fish were not found in lakes with pH's < 6, fish distributional patterns were probably related to historical stocking patterns and the size (area, depth) of lakes. Although small, Lake C-24 was stocked at least 5 times; however, the reasons for the absence of fish in this lake are uncertain and may be related to a lack of spawning streams as well as to the lake's high acidity. With the exception of Lake N-3, young-of-the-year (YOY) trout were observed in shoreline areas or tributary streams of all lakes containing fish, indicating that natural reproduction was maintaining fish populations in these lakes. In addition, these lakes were last stocked so long ago that fish populations must be maintained by natural reproduction. Although most of the fish lakes were connected to perennial streams, the outlet stream for Lake N-3 had dried up in the drought preceding the year this study was conducted. As a consequence, no YOY trout were observed in or near this lake, and the lake's trout population was dominated by older individuals. It is probable that the advent of wet years, as in this past snow year (1992-93), will cause this lake's tributary streams to flow again, creating conditions conducive for golden trout spawning.

Amphibians

In contrast to the survey results for trout, which may depend on past stocking patterns, results for native amphibians, macroinvertebrates, and zooplankton probably provide a clearer picture of the responses of various aquatic animal species to acid conditions. The presence of yellow-legged frog tadpoles in lakes seemed to be, at least partially, predicated on the acidity of lakes. Tadpoles were not observed in any of the acidic lakes (pH < 6), but were commonly observed in non-acidic lakes that lacked fish. Adult frogs, in contrast, were often found in lakes with pH's as low as 5. This difference between tadpoles and adults relative to pH was most striking where acidic and non-acidic lakes occurred in close proximity to each other. Based on distributional differences, it appears that larval amphibians are more sensitive to acid inputs than adults; however, the absence of tadpoles from acidic lakes where adults were present also could have been owing to disruption of mating activities and development (Mathews and Larson 1980). For example, pre-hatching embryonic stages of amphibians are

usually more sensitive to increased acidity than larvae (Pierce 1985; Freda 1986), and this case has been documented in the mountain yellow-legged frog (Bradford et al. 1992). Moreover, acid tolerance of amphibians generally increases as the larvae grow (Pierce 1985; Freda 1986), and transitional stages, such as egg hatching or metamorphosis, appear to be easily disrupted by acid stress (Clark and LaZerte 1985). Determining the exact mechanisms responsible for the absence of tadpoles from acidic lakes will require additional study; however, it is apparent that tadpole distributions are more constrained by acidic conditions than adult distributions.

At present, the mountain yellow-legged frog is relatively abundant in the study area relative to other areas in the Sierra Nevada. The species was recorded in 36 of 104 lakes examined, and occurred in 9 of the 11 designated watersheds (includes A watershed where species was observed, but not in lake A-1; Appendix II). In many other areas of Sequoia and Kings Canyon National Parks, and the Sierra Nevada in general, the distribution of the species is much more sparce, and many populations have disappeared in the past two decades (Bradford et al., in press; Bradford et al., ms. in review).

It is interesting that tadpoles of the mountain yellow-legged frog appear to be adversely affected by pH < 6.0 in the field, whereas survivorship of embryos and tadpoles exposed to a range of pH's in the laboratory for 7 days was not significantly affected by pH's as low as 4.75 (Bradford et al. 1992, 1993). Growth rates of embryos, on the other hand, were reduced when pH was 5.25 and lower. The apparently greater sensitivity in the field may be owing to a number of reasons. One may be that many chemical factors are correlated with low pH (Chapter 2), and these factors may be affecting embryos or tadpoles rather than pH. For example acidic lakes contained concentrations of sulfate and aluminum many times greater than levels used in the laboratory experiments, and both sulfate and aluminum can be toxic to amphibian embryos and larvae (Ireland 1991; Freda 1991). Acid lakes contained a median of 410 μEq/L sulfate (range: 255-616) and a median of 69 μEq/L aluminum (range: 5-107) (Table 2.2), whereas levels in laboratory experiments at similar pH's were approximately 100 μEq/L and 9 μEq/L, respectively (Bradford et al. 1992, 1993). Other possible explanations for the apparent greater sensitivity in the field include: one-time sampling in the field may miss extreme pH depressions; only a restricted part of the mountain yellow-legged frog life cycle was examined in laboratory experiments; and laboratory experiments do not re-create the host of conditions faced by embryos and larvae in the field.

Marcroinvertebrates and Zooplankton

The species compositions of zooplankton and macroinvertebrate assemblages in the study lakes were similar to those recorded for other lakes in the High Sierra (Stoddard 1987, Melack et al. 1989). Among the zoobenthos, only limnephilid caddis larvae, particularly Hesperophylax, appeared to be affected by acidic conditions. These caddis larvae were absent from lakes with pH's < 6, but were commonly collected in non-acidic lakes lacking fish. The distributions of other invertebrate taxa, however, were unrelated to lake acidity. Previous survey and experimental studies in the Sierra also have found little relationship between the distributions or abundances of macroinvertebrates and pH; however, previous surveys only examined a restricted range of pH values (>6.3) and experimental studies examined responses of the infauna at the bottom of lake enclosures (Melack et al. 1987, 1989; Barmuta et al. 1990). Our survey results extend this lack of a relationship between macroinvertebrate distributions and lake acidity to a wider range of pH values and to epibenthic and water column taxa.

Macroinvertebrate taxa identified as sensitive to acidic conditions in previous studies, such as baetid mayflies (Hopkins et al. 1989), amphipods (Mills and Schindler 1986), and sphaerid clams (Okland and Okland 1980, 1986), were not found in acidic lakes in the present study; however, their infrequent collection in non-acidic lakes precluded rigorous statistical testing. Sialis larvae are generally thought to be tolerant of acidic conditions but were only collected from non-acidic lakes, and mayflies, in general, are thought to be sensitive to acidic conditions, but Ameletus was collected from several acidic lakes (Sutcliffe and Carrick 1973, Grahn et al. 1974, Friberg et al. 1980, Hagen and Langeland 1973). These results exemplify some of the difficulties in extrapolating from previous studies, conducted in other geographical areas, to High Sierra conditions. In general, it appears that macroinvertebrate taxa sensitive to acidic conditions are rare in High Sierra lakes.

In contrast to macroinvertebrates, zooplankton assemblages appeared to show a variety of responses to increased acidity. Common microcrustacean taxa, such as Diaptomus eiseni, D. shoshone, D. signicauda, and Daphnia spp., were rare or absent in acidic lakes (pH's < 6), but were commonly collected in non-acidic lakes lacking fish. There also appeared to be differences in the responses of these sensitive taxa, because Diaptomus shoshone was collected in low densities from a lake with pH 5.3, Diaptomus signicauda was collected from lakes with pH's 5.3 and 5.7, but the lowest pH for waters from which Daphnia was collected was 6.3. In contrast common chydorid cladocerans (Chydorus sphaericus) and rotifers (Keratella spp., Polyarthra sp., Trichotria) were

commonly collected in both acidic and non-acidic lakes. Previous surveys of High Sierra zooplankton assemblages (e.g. Stoddard 1987, Melack et al. 1989) found few relationships between the presence or abundances of zooplankton taxa and pH. Again, however, these surveys did not include lakes with pH's < 6.

Experimental studies in large enclosures in a High Sierra lake (Emerald Lake, Barmuta et al. 1990; Melack et al. 1987, 1989) produced results congruent with the results of this study. Diaptomus signicauda and Daphnia rosea declined in abundance when pH was reduced below 5.8-6.0, and these taxa were virtually eliminated below pH's of 5 - 5.2 (see also Marmorek 1984). Furthermore, Daphnia seemed to be slightly more sensitive to acid inputs than Diaptomus. Keratella taurocephala generally increased in abundance as pH declined below 5.6, whereas Chydrous sphaericus and Polyarthra sp. were relatively unaffected by pH manipulations. It is difficult to compare the quantitative results of our experimental studies (Barmuta et al. 1990, Melack et al. 1987, 1989) with the results of this survey because of high variability in the abundance data from the survey. At relatively high pH's density data for sensitive taxa across our fishless lakes ranged from very low or non-existent to very high, indicating that additional factors were affecting the distributions and abundances of these taxa or that our survey data, resulting from sampling at one point in time, did not capture the seasonal range or annual average of abundance data for common taxa. Qualitative agreement between the experimental and survey results, however, was excellent. Daphnia and Diaptomus were absent or nearly absent from acidic lakes, whereas Chydorus, Polyarthra, and Keratella were collected in similar frequencies from acidic and non-acidic lakes. These results corroborate an extensive literature documenting the high sensitivity of Daphnia and Diaptomus (except the tolerant Diaptomus minutus) to acid inputs, and the high tolerance of Chydorus, Keratella, and Polyarthra to acidic conditions (reviewed in Melack et al. 1987, Brett 1989). Although Keratella taurocephala is usually regarded to be more tolerant of acidic conditions than K. cochlearis (Siegfried et al. 1984, Chengalath et al. 1984, Brezonik et al. 1984, Roff and Kwiatkowski 1977), K. cochlearis was collected from more lakes (11) with a wider range of pH (4.86-8.23) than K. taurocephala (3 lakes, pH's 6.53-6.91). In addition, our survey results corroborate an extensive literature showing positive relationships between microcrustacean species richness and pH (see reviews in Melack et al. 1987, Brett 1989). Interestingly, we found no relationship between rotifer species richness and pH.

Impacts of Introduced Trout

The largest, current anthropogenic impact on high-altitude lakes in the Sierra Nevada has resulted from the introduction of exotic fish species. Originally, most High Sierra waters lacked fish, but extensive stocking has resulted in the presence of trout in many High Sierra lakes (Christensen 1977). The results of the present study and others (Melack et al. 1987, 1989) indicate that the introduction of fish has had profound effects on the structure of faunal assemblages in High Sierra lakes. Large and/or mobile, conspicuous taxa, including tadpoles, large-bodied microcrustacean zooplankton, baetid and siphlonurid mayflies, hemipterans (notonectids, corixids), limnephilid caddis larvae, and dytiscid beetles, were rare or absent in lakes containing fish, but were commonly collected in lakes lacking fish (see also Zaret 1980, Bendell and McNicol 1987, Cooper 1988). The disappearance of aquatic amphibians from many parts of the Sierra may be owing to the vulnerability of larval amphibians to fish predation and the widespread introduction of trout to Sierran lakes (Hayes and Jennings 1986); Bradford 1989; Bradford et al., in press). Similarly, large-bodied zooplankton species (maximum size > 2 mm) are generally found only in fishless lakes, whereas small species (maximum size < 1.5 mm) may be found in both fish and fishless lakes (this study) and may actually reach higher abundances in lakes containing fish than in lakes lacking fish (Melack et al. 1989). The introduction of trout results in the decline or elimination of large, mobile, and epibenthic/limnetic macroinvertebrates (large mayflies, hemipterans, limnephilid caddis larvae, dytiscid beetles), shifting dominance to smaller, more cryptic taxa (chironomids, oligochaetes). In some cases outside the Sierra Nevada, the elimination of fish by acidification has resulted in an increase in acid-tolerant macroinvertebrates that are vulnerable to fish predation (e.g. corixids, dytiscid beetles), and the liming of acid lakes and subsequent fish introductions have resulted in the demise of these species (Eriksson et al. 1980, Henrickson et al. 1980, Evans 1989).

Summary of Effects of Lake Acidity and Introduced Fishes

In summary, our surveys of acidic and non-acidic lakes in the Bench Lake/Mt. Pinchot area of Kings Canyon National Park revealed that yellow-legged frog tadpoles (Rana muscosa), limnephilid caddis larvae (Hesperophylax), and large microcrustaceans (Daphnia, Diaptomus) were rare or absent in lakes having pH's < 6, but were commonly collected from lakes with pH's ≥ 6. These results have augmented previous survey data to include more acidic conditions. Our zooplankton results show excellent

qualitative agreement with the results of previous small-scale experimental studies; however, quantitative comparisons were hampered by high variability in the survey data. Trout belonging to four species were collected from or observed in a small proportion of the study lakes, and trout distributions appeared to be related to historical stocking patterns. The distribution of trout appeared to have large effects on the distributions and abundances of amphibian and invertebrate taxa, with large, mobile, and conspicuous taxa being rare or absent in trout lakes, but relatively common in lakes lacking trout. The results suggest that increased acidification of High Sierra lakes will result in the elimination of larval amphibians, large microcrustaceans, and a few macroinvertebrates from lakes, and a decline in microcrustacean species richness. At the current time, however, the most profound human impacts on aquatic communities in the High Sierra appear to be related to historical and on-going stocking of exotic fish species into High Sierra waters.

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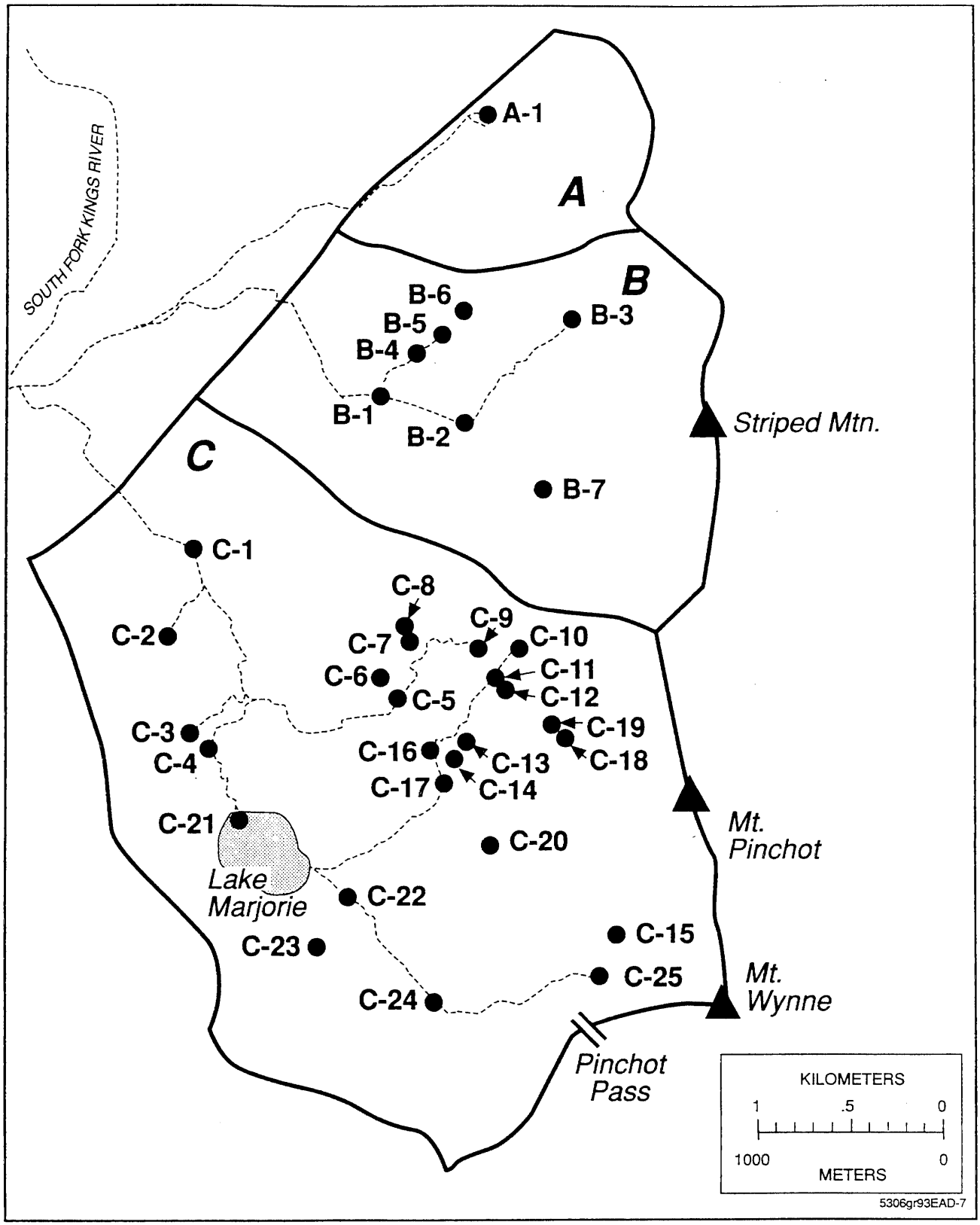
GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

ANC	Acid Neutralizing Capacity
CARB	California Air Resources Board
EC	Electrical conductivity; specific conductance
NPS	National Park Service
WLS	Western Lakes Survey (Landers et al. 1987; Eilers et al. 1989)
YOY	Young-of-year
Z_{max}	Estimated maximum lake depth

Appendix I

Location and Identification of Individual Lakes within Designated Watersheds

(Base maps are Figure 1.1 and U.S. Geological Survey 7 1/2' quadrangle, Mt. Pinchot, Calif., Provisional Edition, 1985.)


SOUTH FORK KINGS RIVER
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B-4
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B-2
Striped Mtn.
C
B-7
C-1
C-8
C-2
C-7
C-9
C-10
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C-11
C-5
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C-19
C-4
C-16
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C-17
C-14
C-21
C-20
Mt.
Pinchot
Lake
Marjorie
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C-25
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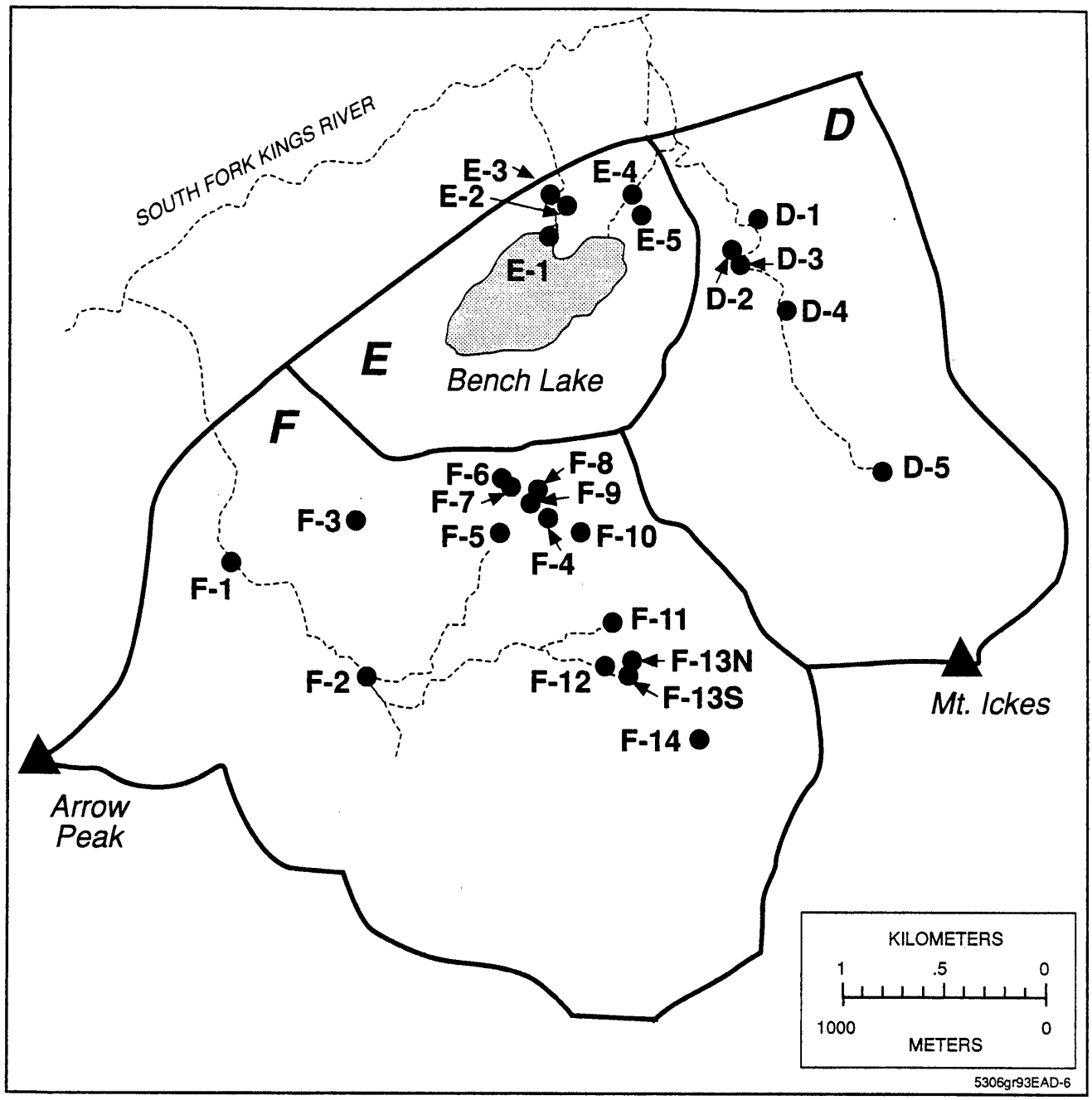
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Bench Lake
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F-7
F-9
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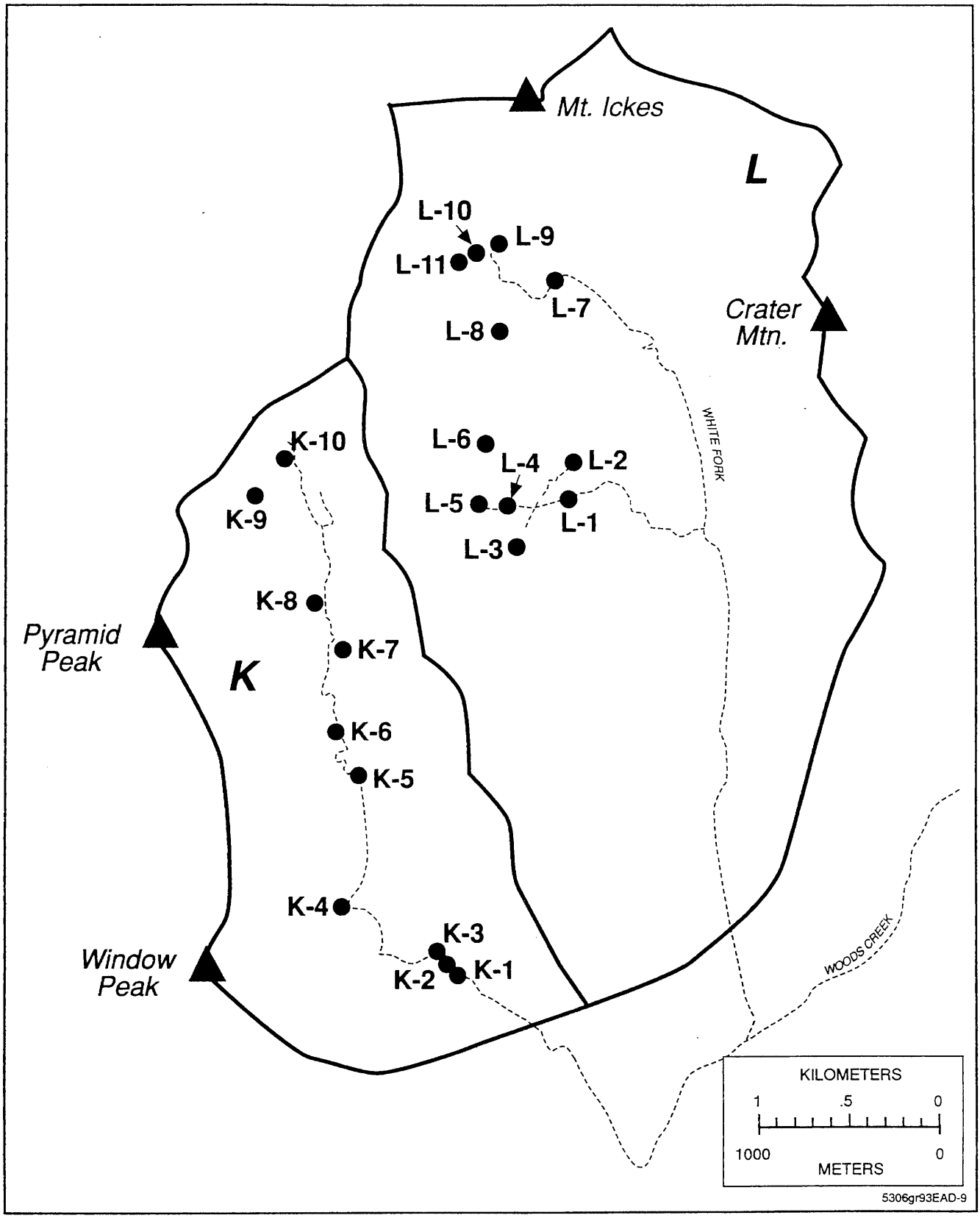
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Crater
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WHITE FORK
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L-5
L-1
L-3
K-8
Pyramid
Peak
K-7
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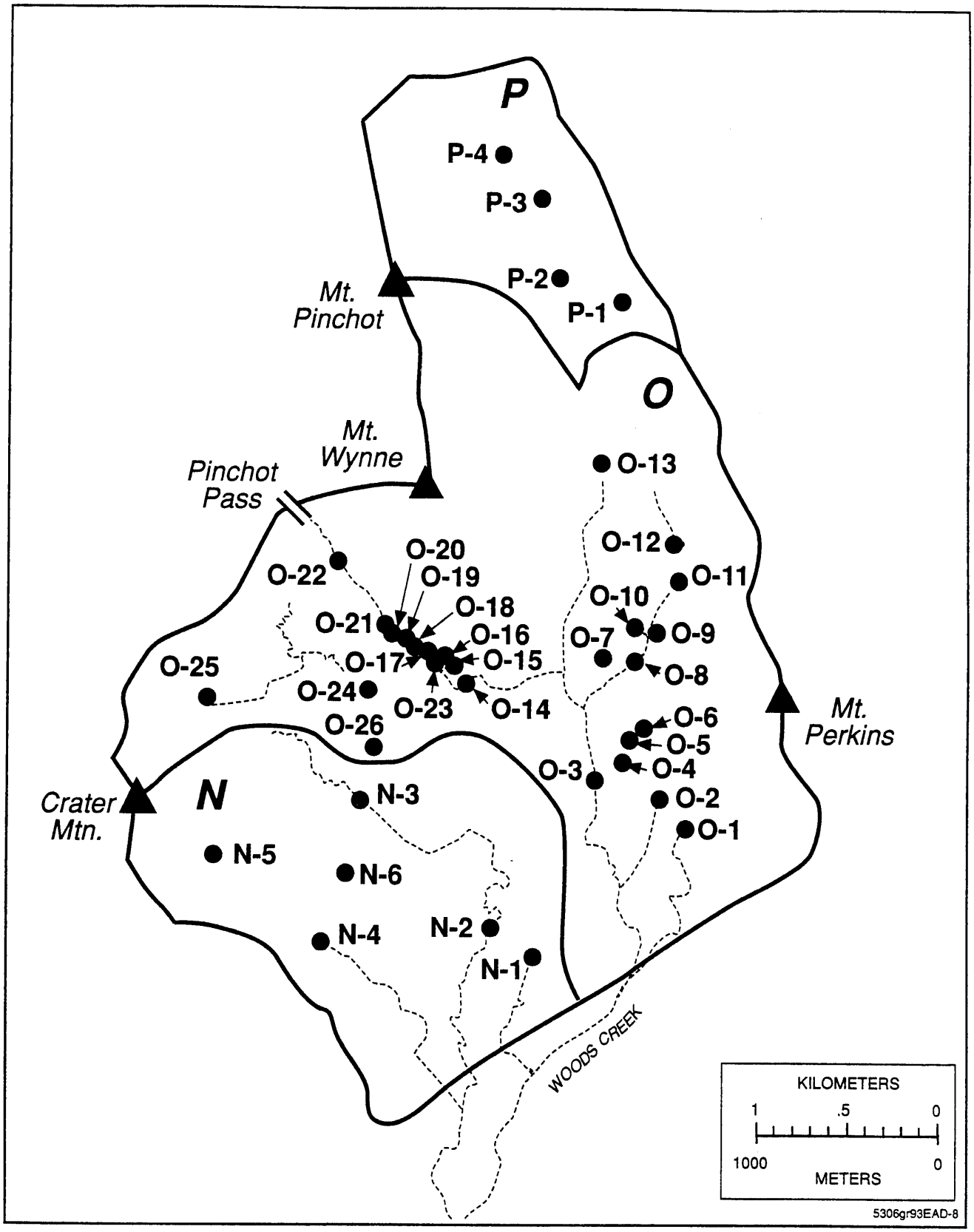
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Perkins
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Crater
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Appendix II

Data for Water Chemistry, Amphibians, and Fish in the 104 Lakes in the Synoptic Survey

Lake ID	Date (m/d/y)	Time (hrs)	Elev. (m)	Est. Depth (m)	Water Temp. (C)	Sample Temp. (C)	pH	Cond. (uS/cm)	R.m.	P.r.	Fish	Remarks
A-1	7/4/92	0945	3410	0.8	7.8	18.3	7.57	34.80	0	0	0	
B-1	7/4/92	1300	3470	>=10	9.4	17.8	7.49	23.70	2	0	1	
B-2	7/4/92	1230	3471	>=10	8.3	17.2	7.52	24.60	2	0	1	Fish observation derived from fishermen.
B-3	7/4/92	1125	3538	>=10	7.8	17.1	7.01	14.83	0	0	0	
B-4	7/4/92	1055	3498	0.5	10.0	17.9	6.52	3.83	0	0	0	
B-5	7/4/92	1040	3500	2.5	11.1	18.3	6.36	3.14	3	0	0	
B-6	7/4/92	1020	3490	4.5	12.8	17.6	6.96	7.28	3	0	0	
B-7	7/4/92	1200	3525	1.8	5.0	18.0	7.60	38.10	0	0	0	
C-1	7/4/92	0905	3295	3	8.9	17.1	7.22	31.30	0	0	1	
C-2	7/4/92	1040	3350	3	13.9	16.6	7.74	101.90	3	0	0	Pseudacris in nearby pond
C-3	7/4/92	1020	3370	>=3	10.6	17.7	7.25	28.70	0	0	1	
C-4	7/4/92	0955	3370	>=5	10.0	17.2	7.15	28.50	0	0	1	
C-5	6/29/92	1750	3515	>10	9.4	6.2	7.23	9.68	0	0	1	
C-6	6/29/92	1740	3545	0.5	8.9	4.9	7.34	8.71	0	0	0	
C-7	6/29/92	1730	3540	2.5	11.1	5.2	6.87	3.91	1	0	0	
C-8	6/29/92	1715	3545	<0.5	11.1	5.5	7.16	5.05	0	0	0	
C-9	6/29/92	1700	3585	4	10.0	6.3	7.36	10.45	1	0	0	
C-10	6/29/92	1610	3600	5	10.0	6	7.56	20.20	3	0	0	
C-11	6/29/92	1640	3595	3	10.0	7.5	7.65	15.65	3	0	0	
C-12	6/29/92	1630	3595	2.5	7.8	5.9	7.46	25.20	0	0	0	
C-13	6/29/92	1500	3555	1.5	7.2	6.6	7.36	18.70	0	0	0	
C-14	6/29/92	1450	3552	1.5	6.7	4.6	7.10	20.80	0	0	0	
C-15	6/29/92	1240	3675	1	7.8	3.7	7.15	11.80	0	0	0	
C-16	6/29/92	1440	3550	2	9.4	6.6	7.40	15.56	0	0	0	
C-17	6/29/92	1415	3550	4	11.1	6.6	7.40	14.80	3	0	0	
C-18	6/29/92	1530	3635	4	6.7	6.1	7.35	18.85	0	0	0	
C-19	6/29/92	-	-	0.5	-	-	-	-	-	-	-	Small and nearly dry.
C-20	6/29/92	1345	3615	1.5	10.6	6	6.11	1.97	0	0	0	
C-21	6/29/92	0900	3393	>10	7.8	4.1	7.28	26.60	0	0	1	
C-22	6/29/92	1035	3425	>5	11.1	4.1	5.49	40.50	2	0	0	
C-22	7/3/92	1730	3425	>5	12.2	7.9	5.38	43.20	2	0	0	Repeat sample on different date.
C-23	6/29/92	1010	3430	5	8.9	3.6	7.47	43.70	0	0	0	
C-24	6/29/92	1120	3485	>5	8.9	6.4	5.22	46.00	0	0	0	
C-25	6/29/92	1220	3645	4	8.3	3.9	6.99	8.12	0	0	0	

Lake ID	Date (m/d/y)	Time (hrs)	Elev. (m)	Est. Depth (m)	Water Temp. (C)	Sample Temp. (C)	pH	Cond. (uS/cm)	R.m.	P.r.	Fish	Remarks
D-1	7/1/92	1045	3270	3	12.8	9.5	7.00	21.60	0	0	1	
D-2	7/1/92	1115	3270	0.5	13.9	8.4	5.96	6.71	2	1	0	
D-3	7/1/92	1100	3270	2	10.6	8.8	6.87	23.00	0	0	1	
D-4	7/1/92	1140	3275	>5	10.6	8.7	6.88	23.20	0	0	1	
D-5	7/1/92	1230	3470	>10	8.3	8.5	6.86	20.70	0	0	0	
E-1	6/30/92	1130	3218	>10	12.8	4.6	7.19	14.95	0	0	1	
E-2	6/30/92	1100	3215	3	12.8	4.7	7.35	14.95	0	0	1	
E-3	6/30/92	1115	3210	0.5	13.3	5.2	7.29	15.04	2	0	1	Only one small metamorphosed Rana, near inlet.
E-4	6/30/92	1030	3230	2.5	13.3	5.3	6.60	6.48	3	1	0	
E-5	6/30/92	1045	3235	1.5	14.4	5.2	6.27	4.08	0	1	0	
F-1	6/30/92	1330	3130	2.5	11.7	4	5.38	53.00	2	0	0	Only two Rana adults.
F-2	6/30/92	1430	3210	>3	12.2	4	5.26	65.10	2	0	0	Only three Rana adults; Pseudacris in nearby pool.
F-3	7/1/92	1605	3290	3	15.0	7	6.93	9.18	0	1	0	
F-4	7/1/92	1430	3470	5	12.2	6.2	7.41	14.15	3	0	0	
F-5	7/1/92	1530	3465	0.4	15.6	6.1	7.42	10.51	0	0	0	
F-6	-	-	-	-	-	-	-	-	-	-	-	Dry
F-7	7/1/92	1520	3470	1	15.0	5.9	8.96	11.46	0	0	0	
F-8	7/1/92	1510	3470	1	15.6	5.5	8.52	8.38	2	0	0	
F-9	7/1/92	1500	3470	1.8	15.6	5.2	7.45	5.00	2	0	0	
F-10	7/1/92	1415	3470	3	17.8	4.9	7.90	29.20	3	0	0	
F-11	6/30/92	1815	3475	4	-	4.1	6.22	26.60	1	0	0	
F-12	6/30/92	1700	3478	1.5	13.3	4	7.75	85.80	2	0	0	
F-13N	6/30/92	1800	3480	4	11.1	4	5.83	30.50	0	0	0	Four Rana adults in nearby pool.
F-13S	6/30/92	1715	3480	2	12.8	4	7.22	29.60	3	0	0	Single lake on USGS map is two lakes (F-13N & F-13S).
F-14	6/30/92	1730	3520	10	8.9	3.6	5.48	23.30	0	0	0	
K-1	7/1/92	1620	3152	3	13.9	7.3	7.07	7.94	0	0	1	
K-2	7/1/92	1615	3154	1	13.9	7.2	7.00	7.65	0	0	1	
K-3	7/1/92	1610	3155	5	15.0	7.5	7.24	7.95	0	0	1	
K-4	7/1/92	1530	3240	>=10	12.2	7.1	6.87	6.28	0	0	0	Large lake, may have fish. Psued. nearby.
K-5	7/1/92	1440	3365	0.5	11.7	7.2	6.83	7.88	0	0	0	
K-6	7/1/92	1430	3390	2.5	11.7	7.9	6.92	7.16	0	0	0	

Lake ID	Date (m/d/y)	Time (hrs)	Elev. (m)	Est. Depth (m)	Water Temp. (C)	Sample Temp. (C)	pH	Cond. (uS/cm)	R.m.	P.r.	Fish	Remarks
K-7	7/1/92	1330	3450	4.5	12.8	6.8	7.55	15.29	0	0	0	
K-8	7/1/92	1315	3455	7.5	11.1	7.4	6.85	6.73	0	0	0	
K-9	7/1/92	1240	3620	4	8.9	6.4	6.97	9.50	0	0	0	
K-10	7/1/92	1225	3635	4	10.0	7	7.05	15.53	0	0	0	
L-1	7/2/92	1615	3388	>=10	13.9	9	6.70	10.82	0	0	0	
L-2	-	-	-	-	-	-	-	-	-	-	-	Dry
L-3	7/2/92	1600	3395	5	14.4	10	6.85	8.61	0	0	0	
L-4	7/2/92	1545	3390	1.3	15.0	9	6.99	13.16	0	0	0	
L-5	7/2/92	1535	3395	3	12.8	10.3	6.83	10.79	0	0	0	
L-6	7/2/92	1520	3490	2	12.8	10.1	6.64	12.28	0	0	0	
L-7	7/2/92	1310	3470	1.3	15.0	11	5.04	57.60	0	0	0	
L-8	7/2/92	1440	3495	4	11.7	9.9	6.44	26.00	0	0	0	
L-9	7/2/92	1400	3530	1	18.3	10.1	8.57	43.60	0	0	0	
L-10	7/2/92	1410	3527	0.5	20.0	9.7	5.40	26.70	0	0	0	
L-11	7/2/92	1425	3535	1.3	11.1	9.7	5.64	24.50	0	0	0	
N-1	7/2/92	1530	3310	3	18.3	10.7	8.56	54.50	3	0	0	
N-2	7/2/92	1510	3310	0.2	24.4	13.7	8.95	55.50	0	0	1	Pseudacris nearby.
N-3	7/2/92	1250	3490	>8	15.6	12.7	7.39	27.60	3	0	1	Rana tadpoles in shallow rocky "lagoon".
N-4	7/2/92	1435	3390	>8	10.0	13.2	7.33	22.20	0	0	0	
N-5	7/2/92	1405	3550	>5	11.7	13	7.43	16.75	0	0	0	
N-6	7/2/92	1320	3550	0.5	15.6	12.2	6.26	3.55	0	0	0	
O-1	7/3/92	1545	3375	3	14.4	8.3	6.90	4.77	3	0	0	
O-2	7/3/92	1530	3370	6	14.4	8	7.76	10.56	3	0	0	
O-3	7/3/92	1420	3415	1.5	12.8	8.1	7.52	23.60	0	1	0	
O-4	7/3/92	1515	3385	1.3	15.0	8.1	6.62	3.64	0	0	0	
O-5	7/3/92	1505	3390	1.5	14.4	8	8.19	20.10	0	1	0	
O-6	7/3/92	1500	3395	0.3	19.4	8.2	7.91	40.40	0	1	0	
O-7	7/3/92	1350	3428	1.3	13.3	7.9	8.06	38.00	2	0	0	Only 1 adult Rana
O-8	7/3/92	1345	3430	2.5	20.0	7.8	9.08	25.40	0	0	0	
O-9	7/3/92	-	-	-	-	-	-	-	-	-	-	Dry
O-10	7/3/92	-	-	-	-	-	-	-	-	-	-	Dry

Lake ID	Date (m/d/y)	Time (hrs)	Elev. (m)	Est. Depth (m)	Water Temp. (C)	Sample Temp. (C)	pH	Cond. (uS/cm)	R.m.	P.r.	Fish	Remarks
O-11	7/3/92	-	-	-	-	-	-	-	-	-	-	Dry
O-12	7/3/92	1240	3510	0.3	10.6	7.6	6.27	5.36	0	0	0	
O-13	7/3/92	1215	3550	4	12.8	7.8	9.34	52.70	0	0	0	
O-14	7/3/92	1255	3430	1	15.6	10.9	7.34	16.68	2	0	0	
O-15	7/3/92	1300	3450	1	15.0	10	6.87	6.48	0	0	0	
O-16	7/3/92	1230	3450	2	15.0	8.9	7.04	8.96	3	0	0	
O-17	7/3/92	1215	3450	1.5	15.6	10.1	7.21	9.55	3	0	0	Uncertain ID of lake based on map.
O-18	7/3/92	1155	3450	1.3	16.1	10	7.15	13.04	3	0	0	
O-19	-	-	-	-	-	-	-	-	-	-	-	Appears to part of O-20.
O-20	7/3/92	1140	3450	3	13.3	10.2	7.14	12.63	3	0	0	
O-21	7/3/92	1125	3450	4	13.9	10.6	7.18	12.84	3	0	0	
O-22	7/3/92	1100	3510	3	12.8	9.8	7.18	11.85	0	0	0	
O-23	7/3/92	1325	3450	0.5	18.3	9	6.77	5.92	2	0	0	
O-24	7/3/92	1415	3490	0.8	17.8	9.5	7.28	18.20	2	0	0	
O-25	7/3/92	1450	3610	>10	10.6	9.4	6.57	13.11	0	0	0	
O-26	7/2/92	1210	3510	1	17.2	11	6.66	15.57	0	0	0	
P-1	-	-	3710	-	-	-	-	-	-	-	-	Above known elev. limit of amphibians (>3660 m).
P-2	-	-	3730	-	-	-	-	-	-	-	-	Above known elev. limit of amphibians (>3660 m).
P-3	-	-	3672	-	-	-	-	-	-	-	-	Above known elev. limit of amphibians (>3660 m).
P-4	-	-	3690	-	-	-	-	-	-	-	-	Above known elev. limit of amphibians (>3660 m).

Notes:

Elev. = elevation derived from USGS 7 1/2' quad. (Mt. Pinchot).

Est. Depth = maximum depth estimated visually from shore.

Water Temp. = temperature of water when sample taken.

Sample Temp. = temperature of water sample when pH measured.

Cond. = Uncorrected specific conductance; actual conductance = uncorrected conductance x 0.9772 - 2.159.

R.m. = Rana muscosa (0 = absent; 1 = tadpoles only; 2 = "adults" [i.e., metamorphosed individuals] only; 3 = tadpoles and adults present).

P.r. = Pseudacris regilla (0 = absent; 1 = tadpoles only)

Fish (0 = absent; 1 = present).

Appendix III

Water Chemistry Data for the 33 Lakes in the Detailed Survey, the 10 Lakes Sampled Three Times, and Several Other Sites

code	date	conduct.	pH	alkal.	Cl	NO3	SO4	NH4	Ca	Mg	Na	K	H+	Al	Al	∑+/∑-
		uS cm-1	UCSB lab		ueq. l-1	ueq. l-1	ueq. l-1	uM	ueq. l-1	ueq. l-1	ueq. l-1	ueq. l-1	ueq	ppb	ueq l-1	
L-7	7/2/92	62.2	4.82	-7	3.4	7.3	460	0.2	239	97	41.5	16	15.19	961	106.9	1.10
E1	6/30/92	16.9	6.93	88	N.F.S.									4	0.445	
F-1	6/30/92	60.1	4.86	-1	7.6	9.2	436	1	215	130	40	18	13.86	2.2	0.245	0.92
F2	6/30/92	72.6	4.8	0	3.9	10.8	581	0.2	243	158	40	18.5	15.91	1065	118.4	1.00
F-4	7/1/92	14.9	6.82	68	3.7	0	43.9	0.3	99	8.4	16.7	4.7		8.7	0.967	1.13
F-11	6/30/92	29.3	5.87	11	8.5	14	198	0.6	134	37.2	32.1	13.6	1.36	40.8	4.537	0.97
F-14	6/30/92	26.1	5.24	2	N.F.S.								5.79	100	11.12	
C-2	7/4/92	110	7.41	246	8.8	0.3	608	0.5	448	24	248	10		40	4.448	0.85
C-21	6/29/92	30	6.65	66	3.4	3.6	159	0	194	37	21.7	7		22.4	2.491	1.13
C-22	7/3/92	49	5.11	3	3.6	11.7	350	0.3	175	102	22.5	9	7.81	482	53.59	1.01
C-24	6/29/92	51	4.83	-2	3.9	12.4	396	0.3	196	110	24.5	9	14.85	623	69.27	1.03
B-1A	8/15/92	26.2	7.28	108	6	5.6	98.6	0.6	195	20.8	22	10.7		9.7	1.079	1.15
B-1B	8/15/92	26.4	7.43	124	4.4	5	97	0.3	196	19.7	22	10.7		7.8	0.867	1.08
B-5	8/15/92	5.3	6.33	15	3.8	1.2	12.7	0.4	14.3	3.3	9.1	4.5		8.5	0.945	1.00
C-2	8/12/92	145	8.23	322	8	0.1	869	0.1	972	30	322	10		22.1	2.457	1.11
C-4	8/11/92	31.6	6.83	122	4.1	2.3	178	0	216	35.8	24.3	7.1		21.4	2.379	0.93
C-5	8/13/92	10.9	6.9	56	2.7	0.3	22.7	0	59.4	11	16.2	6.9		5.9	0.656	1.15
C-10	8/13/92	22.7	7.38	130	3.6	1.4	42.3	1.2	189	15.3	11.9	7.9		9.9	1.101	1.28
C-17	8/13/92	22	7.2	99	3.4	1.6	57.2	0.8	143	16.7	14.3	8.9		28.4	3.158	1.16
C-21	8/11/92	30.7	6.9	62	3.4	2	190	0	194	35	21.6	6.8		12.2	1.357	1.01
C-22	8/12/92	47.5	5.27	-0.4	5.2	10.8	406	1	204	104	30	11	5.41	197	21.9	0.89
C-23	8/12/92	74.4	7.1	215	23.5	26	367	0.8	530	35	20.5	12.5		9.2	1.023	0.95
C-24	8/12/92	57.6	4.73	-14	4.7	12.4	442	1	185	117	27.5	9	18.68	675	75.05	0.94
F1	8/21/92	68.4	5	-3	4.4	10.3	578	0.3	247	146	49	22.5	10.05	479	53.26	0.89
F2	8/21/92	75.8	4.86	0.5	4.7	9.7	560	0.3	288	162	55	24.5	13.86	663	73.72	1.07
F4	8/22/92	17.5	6.57	73	5.7	0.2	57.7	0.3	120	9.3	21	5.2		11.5	1.279	1.15
F11	8/22/92	33.8	6.24	15	6.5	10	252	N.E.S	157	42	38.5	17		28	3.113	
F12	8/23/92	120.8	7.59	276	7.7	0.2	820	1.2	787	104	93	28		50	5.56	0.92
F13NA	8/23/92	44.6	5.77	5	4.7	15	338	0.5	193	59	52	25	1.71	68.1	7.572	0.93
F13s	8/23/92	41.6	6.62	50	3.7	3.8	273	2.8	242	41.5	35	17		30.6	3.402	1.03
F13NB	8/23/92	44.5	5.64	-0.5	4.7	15.4	348	0.9	193	57	51	25	2.31	65.7	7.305	0.91
F14	8/23/92	31.8	5.3	1	4.7	25.8	250	0.8	142	39.5	28.5	15.5	5.05	77.7	8.639	0.86
E1	8/19/92	16.6	6.91	94	3.7	2	46.6	0.6	115	6.4	25	5.3		9.7	1.079	1.05
E4	8/20/92	9	6.53	44	8.8	0.1	17.5	0.4	39.4	7.4	24.9	6		78.5	8.728	1.23
N3	8/24/92	33.5	6.93	91	2.6	0.2	175	0.2	199	27.4	59.5	7.8		45.7	5.081	1.11
O-8	8/24/92	29.8	7.23	200	2.3	0	48	0	243	21.1	15.9	8.2		24.5	2.724	1.16
O-21	8/24/92	15.2	6.9	77	2.2	0.2	38.5	0	88.5	14.7	25	7.4		53.5	5.949	1.20
D4	8/20/92	37	6.72	43	4.2	10.2	232	0	242	15.6	30	4.1		47.5	5.282	1.03
D5	8/20/92	24	6.46	29	5.5	22.8	119	0.6	162	11.4	20.7	4.9		19.3	2.146	1.14
L-1A	8/30/92	13	6.65	30	2.6	1.6	69.3	0.2	74.5	8.1	17.4	6.3		27.4	3.047	1.06
L-1B	8/30/92	13	6.64	26	2.6	1.6	67.2	3.2	71	8	16.9	6.3		31.2	3.469	1.12
L-7	8/30/92	82.5	4.72	-6	11.1	8.3	620	0.6	272	132	63	20	19.12	599	66.6	0.90
L-8	8/30/92	52.5	6.64	49	5.7	9.9	365	0.1	288	55	51.5	18		75.8	8.428	0.98
L-9	8/30/92	54.9	7.02	86	4.2	11.62	334	1.1	345	54	11.4	2.4		33.1	3.68	0.96
L-11	8/30/92	40.4	5.96	6	7.72	26.24	278	0.6	216	43.5	40	14.8	1.11	47.9	5.326	1.01

code	date	conduct.	pH	alkal.	Cl	NO3	SO4	NH4	Ca	Mg	Na	K	H+	Al	Al	Σ+/Σ-
		uS cm-1	UCSB lab		ueq. l-1	ueq. l-1	ueq. l-1	uM	ueq. l-1	ueq. l-1	ueq. l-1	ueq. l-1	ueq	ppb	ueq l-1	
O-7	9/1/92		N.U.S.		7.9	0	40	0	438	36.9	31.2	21.6				
P3	9/1/92		N.U.S.		2.9	1.8	37.2	0	180	10.3	7.2	6.5				
F1	9/25/92	73.3	5.3	55	4.6	8.5	549	1.2	282	163	54	26.5	5.05	932	103.6	1.03
F2	9/25/92	83.3	4.94	-5	5	9.6	708	0.4	318	186	62	26.5	11.53	1172	130.3	1.02
F4	9/25/92	20.6	6.55	86	4	0.4	65	0.5	106	11	17	5.1		4.9	0.545	0.90
F11	9/25/92	35.2	6.2	15	4.8	7.2	268	0.5	158	45	36	17.5		23.3	2.591	0.88
F11A	9/25/92	34.5	6.15	22	4.2	7.1	271	0.8	160	44	44	24		28.9	3.213	0.91
F14	9/25/92	34.5	5.46	-1	4.5	26	260	0.8	157	44.5	27.8	15.2	3.49	89.6	9.963	0.89
C2	9/26/92	159.3	7.17	341	10	0.5	920	1	1020	33	316	12.2		39.8	4.425	1.09
C21	9/26/92	30	6.79	64	6.2	2.6	172	0.6	177	35	21	7.4		18.2	2.024	0.98
C22	9/26/92	48.3	6.05	10	4.3	6.9	362	0.6	229	95	34	11		608	67.6	1.14
C24 (L	9/26/92	61.2	4.84	-12	4	12.1	512	1.2	207	132	31	8.9	14.51	1143	127.1	0.99
E1 Bei	9/25/92	17.5	6.79	87	4.6	0.2	45.5	0.9	107	7	23	6		93	10.34	1.12
F drair	9/25/92	523	4.29		14.5	8.4	7475	170.6	1730	1910	126	50	51.32	18130	2016	0.81
F2 inflow 3														13.9	1.546	
F2 inflow 4														1581	175.8	
F2 upper meadow inflow5														249	27.69	
F2 upper meadow inflow 2														1341	149.1	
F2 upper meadow														1427	158.7	
F2 outlet														1016	113	
F2 inlet 3														21.4	2.379	
C24 acid spring														4630	514.8	
F2 inlet 4																
N.E.S.=Not enough sample																
N.F.S. = No filtered sample																
N.U.S.= No unfiltered sample																

Appendix IV

Geologic Controls of Natural Acidification of Alpine Lakes in the Eastern Sierra Nevada

Contract No. A132-192

Gail Mahood
Cheryl Gansecki

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Supporting Study to:

Distribution of Aquatic Animals Relative to Naturally Acidic Waters in the Sierra Nevada

Contract No. A132-173

GEOLOGIC CONTROLS ON NATURAL ACIDIFICATION OF ALPINE LAKES IN THE EASTERN SIERRA NEVADA

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ABSTRACT

Oxidation of the mineral pyrite during surficial weathering is the source of acid water that results in naturally acidified lakes in the Mt. Pinchot region of the Sierra Nevada, California. The presence of pyrite is not sufficient to acidify the surface waters, as evidenced by the lack of correlation between the amount of exposed pyrite and the acidity of the lake waters and by the fact that some drainage basins containing small amounts of pyrite-bearing rocks have lakes with normal pH values. Geomorphologic and geohydrologic features specific to each basin control whether surface waters are acidified. Conditions that lead to mechanical reduction in grain size of pyrite-bearing rocks (e.g., crushing in a rock glacier and in a fault zone) promote acidification, whereas those that lead to exposure of fresh surfaces on pyrite-free lithologies (e.g., active rocks falls and large talus slopes resulting from steep alpine glacial topography) promote acid-neutralizing weathering reactions. Adjacent lakes within the same drainage basin can have greatly different pH (and therefore biota) because such geomorphologic conditions can vary on scales of less than a kilometer and because pyrite is largely restricted to specific lithologies (hydrothermally altered metamorphic rocks and small pods of leucocratic granite). Where acid streams are diluted by inflows of neutral water, the resulting increase in pH leads to the precipitation of white rinds of hydrous aluminum sulfate on the rocks of the streambed. Large streams and paternoster lakes at the lowest elevations tend to be nearly neutral, because the localized inputs of acid water from pyrite-bearing rocks are overwhelmed by neutral waters that characterize the bulk of larger drainage basins.

INTRODUCTION

In order to establish the effect of airborne pollution on the acidity of high-altitude surface waters, it is necessary to establish background pH levels of alpine lakes. Field teams conducting surveys for amphibians, fish, macroinvertebrates, and water chemistry under contract to the California Air Resources Board (CARB) discovered in 1991 that there are both acidic and non-acidic lakes in the Bench Lake/Mt. Pinchot area of Kings Canyon National Park in the eastern Sierra Nevada. Given that the lakes occur in a small area, over which contributions to lake acidity from air pollution, if any, are assumed essentially constant, the acidification of some of the lakes is thought to be natural. This area thus serves as a natural experiment to determine the effects of lake acidification on biological activity, with an eye toward predicting the likely effects on Sierran lakes if increasing smog inputs from southern California result in increasingly acid precipitation. Geologic mapping of the area at the 1:50,000 scale (Moore, 1963) has identified a wide range of lithologies, with varying potential for acidifying or neutralizing surface waters, and so the area also provides a natural experiment on the influences of bedrock lithology and local geomorphology on the pH of alpine lakes. Identifying these influences was the goal of the study reported here.

General Geology and Geomorphology of the Mt. Pinchot Region

The study area lies within the Kings Canyon National Park in the central Sierra Nevada, eastern California. The lakes and streams studied lie at elevations of 3200-3700 m, with the highest peak, Mt. Pinchot reaching 4113 m. All the area underwent alpine glaciation; most of the lakes are cirque or paternoster lakes. The steep, sparsely vegetated walls of the cirques are commonly footed by talus cones or piles of angular rock fall. The area contains a small amount of moraine and several rock glaciers (Fig. 1). Usually, there are scattered perrenial snow fields on steep north-facing cirque walls, but six years of drought preceding this study resulted in their absence at the time of the field work reported here.

The study area is underlain by granitic plutons of Jurassic and Cretaceous age separated by roof pendants of metasedimentary rocks, including biotite schist, calc-hornfels, pelitic hornfels, quartzite, and minor marble (Moore, 1963). The

Mt. Pinchot region is one of the few in the Sierra Nevada where there are abundant exposures of the roofs of plutons. Together with spectacular felsic dike and sill complexes and the abundance of metapyroclastic rocks in the roof pendant just outside the study area (biotite schist interpreted by Moore (1963) as metamorphosed tuffs and ignimbrites), this suggests that the Mt. Pinchot area preserves the upper parts of these Mesozoic magmatic systems. This accounts for the relative abundance in this area, compared to other parts of the Sierra, of light-colored plutons and pods of true granite.

Moore (1962) identified an area of strong alteration within both metamorphic and granitic rocks, centered about 1 mile west of Crater Mountain (Fig. 1), which contained abundant pyrite. Oxidation of pyrite could lead to acidification of waters in areas draining such bodies, as well as account for elevated levels of dissolved sulfate. Schist and pelitic hornfels can also be a source of pyrite, depending on the conditions under which the original sedimentary rocks formed and the conditions of metamorphism. On the other hand, outcrops of marble provide a source of calcium carbonate that would readily neutralize otherwise acidic water. Silicate rocks also neutralize acid waters through hydrolysis reactions of mafic minerals and feldspars to form clays, though such reactions have a smaller acid-neutralizing capacity than those involving carbonate minerals. Thus the variety of rock types present in the study area may explain why some lakes are acidic and others are not.

Methods

Using the existing geologic map of Moore (1963) and the previous survey of lake acidity as a guide, we spent 10 days in the summer of 1992 examining in greater detail the geology and hydrogeology of the watersheds for selected acid, near-neutral, and neutral lakes in order to identify acid-generating and acid-neutralizing lithologies. We collected samples of pyrite-bearing rocks, hydrothermally altered metamorphic rocks, and coatings that had precipitated in acid-affected streams and at the shore of an alkaline lake. Biological and water-chemistry surveys were undertaken simultaneously by us and by other workers. Subsequently, at Stanford, we employed X-ray diffraction and scanning electron microscopy to determine the composition and mineralogy of the light-colored precipitate found on boulders in acid-effected streams and of soil alteration products of acidification.

RESULTS AND CONCLUSIONS

Source of Acidity

We can *a priori* eliminate acid precipitation as the main source[1] of acidity in the Mt. Pinchot area because lakes separated by less than a kilometer, in the same (granitic) bedrock, can have pH values that differ by several log units, whereas acid precipitation should affect all lakes lying in rocks of similar acid-neutralizing capacity to a similar extent. Rather, the increases in pH observed going downstream in the C and F drainages (Brown, 1993) suggest isolated sources of acidity that strongly affect adjacent lakes, but that either dilution downstream with non-acid water or time-dependent reactions with rocks neutralize the effects of the acid inputs downstream. Our mapping concentrated on establishing the geologic source of acid waters and mapping its distribution. The study area is lacking young volcanic activity and hot springs, so these cannot be the source of acid waters. There has been no mining activity in the area that might give rise to acid mine drainage. Our field work showed that acid lakes were found in association with zones of hydrothermal alteration in metamorphic rocks (Fig. 1). These natural sources of acidity are analogous to acid mine drainage in that they are essentially point sources of sulfuric acid produced by oxidation of fine-grained pyrite in the altered rocks in the weathering environment.

The short duration of our field work did not allow complete remapping of the geology of the area. Thus the geologic map presented in Fig. 1 largely reflects the previous mapping by Moore (1963), with modifications based on our mapping and examination of color air photography. This simplified map illustrates that the general geology consists of three, broad, northwest-trending septa of metamorphic rocks, consisting mostly of biotite schist and calc-silicates, separated by Jurassic and Cretaceous granitic rocks.

The study area is cut by the 148-Ma mafic dikes of the Independence dike swarm (Chen and Moore, 1979). For the most part, these dikes are too narrow to illustrate on the map, but they allow the granitic plutons of the region to be divided

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[1]This does not preclude a background contribution by acid precipitation to the acidity of the lakes and to their sulfate content. We do, however, assume that this contribution would be relatively uniform throughout the study area.

into two groups: an older group that is cut by the mafic dikes and a younger group that is not cut by dikes. Plutons in the study area are mostly granodiorite, with smaller amounts of true granite. Moore (1963) mapped "mafic plutonic rock" in an area near lakes C5 and C17 and in the northern part of the L drainage. That near C5 and C17 is diorite that is extensively hybridized with the surrounding granodiorite. We did not find any clear correlation between the type of plutonic rock in the bedrock and the acidity of lakes. This may be because all the plutonic rocks, from granite to diorite, consist principally of the mineral feldspar, making them all more or less equivalent in their acid-neutralizing capacity.

Based on our brief reconnaissance, there were three map relations that we would alter from Moore's previous mapping that have significance for this project: (1) We believe that what had previously been mapped as an intrusive contact on the east side of the lower F drainage is a high-angle fault that places the Cotter pluton against metamorphic rocks that are locally hydrothermally altered. This faulting is Mesozoic in age, as the fault is cut by the Cartridge Pass and Bullfrog plutons. (2) West of Crater Mountain the pre-Independence-dike-swarm granitic rocks are interleaved with metamorphic rocks on a finer scale than shown on Moore's (and our) map; there are numerous felsic dikes; and some of the metamorphic rocks are metatuffs. Our map outlines where plutonic and metamorphic rocks are dominant, but each contain the other. The importance of these relationships is that it suggests that the study area embodies the roof zone of a plutonic body that was emplaced at relatively shallow levels. (3) We found that marble was a rare rock type and that many rocks that look superficially like marble are in fact quartzite or calc-silicates. Even in the small area shown on Fig. 1 as containing marble, the dominant rock type is calc-silicate. This is significant because it means that the acid-neutralizing capacity that carbonate outcrops or detritus would provide is quite restricted in the study area.

Geologic Controls on the Occurrence of Pyrite

Moore (1963) noted that both granitic and metamorphic rocks centered on an area about 1 mile west of Crater Mountain (i.e., the L drainage of this report, Fig. 1, and the westernmost of the septa) contained abundant disseminated pyrite. Our mapping has confirmed this as the zone of most intense pyritization within

the study area, and shows that it is associated with zones of hydrothermal alteration. We have also found that pyrite occurs additionally along strike to the northwest in the same rocks in the F drainage. There are also broad zones of disseminated pyrite and hydrothermal alteration in the middle of the three septa, but it is largely lacking in the easternmost septa.

Pyrite also occurs as scattered, mm-sized cubes in pods, sills, or dikes of true granite in the C, N, and L drainages. It does not appear that weathering of this pyrite is an important source of strongly acid water.

Moore recognized that whereas the metamorphic wall rocks and the pre-Independence-dike-swarm Twin Lakes and White Fork plutons were pyritized, the post-Independence-dike-swarm Cartridge Pass pluton is not. As is apparent from Fig. 1, this same age relationship holds in the further localities we have identified; post-Independence-dike-swarm plutons are largely free of hydrothermal alteration, and the only noticeable occurrences of pyrite are scattered cubes in small leucogranitic sills or pods. The age of the hydrothermal alteration and the pyritization associated with it can be constrained further by the observation that the mafic dikes that we examined within the area of pyritization in drainage L were not themselves hydrothermally altered. If these dikes are part of the Independence dike swarm, as Moore suggests, the alteration is older than the 148-my age for the swarm. Although most of the hydrothermal alteration is found in metamorphic rocks, in the L and F drainages, the White Fork pluton is also altered, which means that the alteration cannot predate the older suite of plutonic rocks.

The fact that the Mt. Pinchot region represents a relatively shallow paleodepth--that is, one in which metavolcanic rocks and pluton roofs are preserved--may account for the presence and preservation of hydrothermal alteration in the roof pendant. Circulation of heated groundwater to depths of a few kilometers around dikes and shallow plutons may have been the cause of the Jurassic hydrothermal alteration that resulted in argillic alteration and silicification. It is possible that the alteration is a product of a hydrothermal system set up by emplacement of the older suite of granitic plutons.

The geologic control of sources of acidity accounts for the sharp contrasts in pH values of lakes separated by only a few hundred meters. For example, lakes

F11 through F14 are acid-affected whereas nearby lakes F5 through F10 are circum-neutral, because lakes F11-F14 occur in a drainage containing hydrothermally altered rocks, whereas lakes F5-F10 lie just across a low divide in a hydrologically separate basin in which the bedrock is a younger granitic pluton unaffected by the alteration. Geologic control also accounts for the homogeneity of pH values of lakes within some drainage basins. For example, lakes D1 through D5 have nearly identical pH values, because they all lie within a very homogenous part of the unaltered Cartridge Pass pluton.

Geohydrologic Controls on Lake Acidity

Geohydrology also controls the distribution of pH values. For example, lakes F2 and F1 are acid-affected despite lying in basins carved in post-Independence-dike-swarm granodiorites unaffected by pyritization. This is because these lakes receive the bulk of their flow from the large catchment area occupied by the acid-affected marsh at the head of the lower F drainage (Fig. 1). They also receive acid inputs from the stream draining lakes F11 through F14. The surface area of the catchment for near-neutral lakes F4 through F10 is relatively small, so the streams draining this area contribute only a small amount of neutral water to F2 and subsequently F1. Another example of the effect of inflows of differing sizes is the abrupt increase in pH over a distance of only a few hundred meters going downstream from acid-affected lake C22 to near-neutral lake C21. This is because, at the time of the field work, about 90% of the surface water flowing into C21 came from streams draining the basin containing lakes C10 through C17, which is unaffected by hydrothermal alteration, and only about 10% of the flow came from the main drainage from C24 and the area of hydrothermal alteration and pyritization.

In-Stream Neutralization of Acidified Water by Mixing

Field evidence suggests that neutralization of streams and lakes occurs mostly by dilution by near-neutral surface waters derived from drainage basins unaffected by hydrothermal alteration. If one restricts oneself to the bodies of moderate to large size[2] (and in this context, a lake with a 200-m diameter is

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[2]Very small bodies of water--tens of meters on a side and only a meter or two deep--were found during the 1991 survey to have a variety of pH values. Many of these bodies were dry at the time of

"large") the lakes have uniform pH values in drainage basins without pyrite-bearing rocks (e.g., B, D, L1-L6, C5-C19), and, in basins containing signficant volumes of pyrite-bearing rocks, the pH generally decreases downstream from the source of acid water (e.g., C24-C1, F14-F13, and F2-F1; CARB 1991; Brown 1993).

The observed neutralization downstream is unlikely to be a function of time-dependent acid-neutralizing reactions with rocks or surficial deposits because flow rates in streams are high. There would simply not be enough time, given sluggish reaction rates at the ambient temperatures, to produce, for example, the systematic increase in pH that occurs in the few hundred meters distance between lakes C24 and C22 (Fig. 2a in Brown, 1993). This rapid change can be more readily explained as resulting from dilution by near-neutral waters. The two possible sources of near-neutral waters are surface waters and groundwater.

It seems unlikely that dilution takes place largely as a result of influx of groundwater into the streams for two reasons: (1) We found no physical evidence for this process, such as neutral springs or seeps at stream or lake level. (2) Groundwater flow would be limited in this area because surficial deposits are not abundant, and the granitic and metamorphic bedrock would have both low permeability and porosity; thus the potential flux of groundwater into streams is much smaller than the volume of water flowing through the streams at high velocities, so the neutralizing capacity of such groundwater flow on acid-affected streams is small.

In contrast, even during our mid-August field season in a drought year there was abundant surface water; many small streams course down steep slopes in addition to the streams marked on the topographic map. Where these drained areas without significant pyritization, the water had a pH of 7-8, and so mixing of this neutral, low-ionic-strength water with the acid-affected water would raise pH while lowering specific conductance. As neutral sidestreams feed into the main drainage all along its length, the increasing proportion of neutral water in the mixture can account for the progressive increases in pH and declines in specific conductance observed in the C and F drainages and from L7 (adjacent to the area

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our 1992 study. We suggest that studying such small bodies is of little value and that future studies should emphasize lakes of sufficient areal extent and depth that evaporation and biological activity cannot have a significant effect on water chemistry.

of strongest pyritization in the L drainage) to the White Fork (Brown, 1993). Supporting evidence for the importance of surface waters as the neutralizing water is the correlation between the volume of water entering in sidestreams and the rate at which pH increases with distance downstream. For example, pH increases by about 1.7 log units over a distance of about 1 km between C22 and C4, whereas over slightly smaller distances in the F and L drainages the pH changes increases by less than half a log unit. There are many sidestreams that enter the main C drainage from the area draining C5-C18, whereas smaller volumes of water enter the main F and L streams as sidestreams (and in F some of these waters are themselves acid-affected).

The Occurrence of a White Precipitate in Acid-Affected Streams

The most striking evidence for the importance of mixing of near-neutral surface waters with the acid-affected waters on water chemistry is the presence and spatial distribution of a striking white to grey-white to pinkish-white precipitate in the streambeds of the acid-affected drainages C, F, and L. This coating forms on the rocks in the main stream bed where near-neutral sidestreams enter, and is so prominent in the L drainage that the main stream is denoted the White Fork of Woods Creek on topographic maps.

In the L drainage, the precipitate is found for several kilometers below the confluence of the White Fork draining acid-affected L7 and a large near-neutral stream (unmarked on the topo map) draining the northern part of the L basin. The precipitate is thick in the streambed between F2 and F1, and it also occurs locally on the shore of F2 where neutral streams (with no precipitate) enter the acid-affected lake on its east shore. In the C drainage, it occurs in the streambed between lakes C22 and C21. At the outlet of acid-effected Lake C22, the white precipitate is very thin; it is thickest where a stream carrying a large amount of neutral water from lakes C10-C17 enters the main stream, just above C21, Lake Marjorie.

The precipitate does not form in response to evaporation of the acid-affected water. Evidence for this is the absense of a white precipitate in the several feet between the lake level of C22 at the time of the field study and the high water mark. In the case of the C and F drainages, the areal extent of the white

precipitate was much larger than the stream at the time of the survey, suggesting that much of the precipitation took place during periods of higher flow.

The absence of a white precipitate ringing the margins of the acid-affected lakes C24, C22, F14, and F11 also argues against groundwater being the major agent of neutralization of the water. If the precipitate formed by mixing of groundwater and acid lake water, one would expect to see the precipitate in the soil at the margins of the lakes, especially as these areas were exposed during this drought year. In the C, F, and L drainages, we saw that the white precipitate formed on the surface of boulders in the main stream (not in soils at the banks) exactly at the spot where it was joined by large, neutral, sidestreams draining pyrite-free areas. This is very strong evidence that the neutralization is occurring by mixing and dilution with surface waters.

Analyses of the White Precipitate

We analyzed the precipitates that coated rocks in the acid-affected streams using an energy-dispersive X-ray spectrometer attached to a scanning electron microscope (AMR1000 SEM/EDS with Kevex software) in the Center for Materials Research. Coatings were analyzed *in situ* on chips of the host rocks. The electron beam does not penetrate beyond the surface of the sample, so the analysis should not be affected by the composition of the substrate rock. This assumption was tested in several cases by analyzing two rock chips simultaneously: one with a coating and the other without. There were no overlaps apparent in the spectra.

A standardless semi-quantitative analysis of the SEM/EDS data indicates that the precipitates formed in the acid-affected streams are composed of 60 to 80% Al on a cationic basis; the balance consists of S, Si, and Fe (Table 1, Fig. 3). Elements of atomic number less than 11, including O and H, cannot be detected; as a result, quantitative analyses are not possible by this method.

An X-ray powder diffraction (XRD) analysis was conducted using a Rigaku X-ray diffractometer in the School of Earth Sciences at Stanford University on the only surface precipitate for which we had sufficient material, AL-3, from the stream between lakes F2 and F1. The precipitate proved to be amorphous (Fig. 2). The precipitation of poorly ordered compounds, rather than well-crystallized minerals, is expected under the low-temperature conditions of formation.

Given that the precipitates are amorphous, it is not possible to determine directly by what compounds they consist of by XRD analysis. However, a consideration of stability and occurrence of the more than a dozen minerals that form in the system Al_2O_3-SO_3-H_2O narrows the choices. Thermodynamic calculations of the solubilities of aluminum sulfate minerals (Nordstrom, 1982) indicate that alunite ($KAl_3(SO_4)_2(OH)_6$) and, at pH higher than 6, gibbsite ($Al(OH)_3$) should be the stable phases. Alunite has been shown experimentally to precipitate directly from acid sulfate solutions at temperatures $\geq$100°C (Dwivedi, 1973), and Raymahashay (1968) found acid hot springs in Yellowstone with temperatures of 55-73°C precipitating alunite. However, experimental work (Robertson and Hem, 1969) on the titration and coagulation of aluminum sulfate solutions at a lower temperature, 25°C, more applicable to natural conditions in the Mt. Pinchot area, shows that basaluminite ($Al_4(SO_4)(OH)_{10}x5H_20$) is the first precipitate to form. It appears that at low temperatures, precipitation of basaluminite is kinetically favored. This metastable phase will transform to alunite (or gibbsite) over time, given the availability of alkali metals (Na,K) and a suitable catalyst, such as heat or surface area (Nordstrom, 1982).

The presence of a significant S peak in the SEM spectra (Fig. 3) for Mt. Pinchot precipitates requires that a hydrated Al sulfate make up a large proportion of the precipitates. The absence of a peak for K or Na eliminates alunite. The ratio of the heights of the Al and S peaks is about 5:1. Given that some of the Al could be present as gibbsite or kaolinite ($Al_2Si_2O_5(OH)_4$), it suggests that the sulfate mineral has a somewhat lower ratio. This would be consistent with basaluminite ($Al_4(SO_4)(OH)_{10}x5H_2O$), but not with a more sulfate-rich mineral, such as jurbanite ($Al(SO_4)(OH)x5H_2O$), which limits the solubility of Al in solutions with pH values less than 4 (Nordstrom, 1982). As the solubility of amorphous silica (or quartz) is constant at pH below 8, the increase in pH from about 4-5 to about 7 that accompanies the mixing process in the acid-affected streams (Brown, 1993) should not have a significant effect on the solubility of SiO_2 and should therefore not result in precipitation of silica. One possible Si-containing compound stable in this environment is a poorly ordered precursor to the clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$); given the small Si peaks, it may account for a small proportion of the precipitates. Gibbsite ($Al(OH)_3$) is also potentially stable under these conditions. The small peaks for Fe in two of the four

samples suggests the presence of an iron hydroxide. From the foregoing, we suggest that the white precipitate consists largely of poorly formed basaluminite, with small amounts of kaolinite and/or gibbsite, and, in the two Fe-bearing samples, a small amount of iron hydroxide.

Other Occurrences of Precipitates in Acid-Affected Streams

The occurrence of a striking white precipitate in the streams in the Mt. Pinchot area is not unique. Headden (1905a,b) found a white precipitate occurring at the confluence of an acid spring and an alkaline spring in Delta County, Colorado. Analysis of the precipitate yielded a formula of $Al_4(OH)_{10}SO_4x5H_2O$, which corresponds to the mineral basaluminite. Theobald et al. (1963) observed a white precipitate coating the streambed directly below the confluence of a basic stream (pH~8) with an acidic stream (pH~4) draining a mine in Summit County, Colorado. Above the confluence, the acid stream contained high concentrations of dissolved Fe, Al, and sulfate resulting from the oxidation of disseminated pyrite and the consequent leaching of Al from the bedrock. Upon mixing, the pH of the main drainage increased from 4 to 6, and sulfate and aluminum decreased significantly. The white precipitate was found to be amorphous and consist largely of Al, Fe, sulfate, and water, causing them to hypothesize that the precipitate was largely a mixture of aluminum hydroxide and a basic aluminum sulfate. Nordstrom and Hashaw (unpub. data cited in Nordstrom, 1982) have found several localities where the mixing of acid and neutral streams results in a white aluminum sulfate coating in the streambed, and Nordstrom (1982) believes such occurrences are more common than the literature would imply.

Proposed Mechanism for Producing the White Precipitate

These other natural examples of precipitation of a hydrated alumina sulfate where acid waters mix with either neutral or alkaline waters support the conclusion we had reached independently based on field evidence in the Mt. Pinchot region for the importance of mixing of surface waters in neutralizing acid waters and producing the white precipitate. We can also examine the data on the solubilities and stabilities of the minerals found in the precipitates to see if they are consistent with a model involving precipitation due to mixing. The solubility of the various aluminum compounds is a function of potassium and sulfate activity (assuming silica activity is fixed below pH 8 by saturation with

respect to quartz or amorphous silica). Nordstrom (1982) calculated solubility curves as a function of pH for conditions similar to acid rain and to acid mine waters, reproduced here as Fig. 4. This spans the conditions applicable to the Mt. Pinchot area, as the amount of pyrite, and, thereforefore, acidity occurring in this area is much smaller than that observed in areas with acid mine drainage, where pH values can fall to below 1. These calculations show that both basaluminite and gibbsite have minima in their solubility curves around pH 6. Thus increasing the pH from the values of about 5 found in the acid-affected lakes by admixing water from sidestreams with pH of 7-8 could result in precipitation. Measured pH values in streams where precipitate occurs are about 7, consistent with such an explanation. Such an increase in pH could also lead to the precipitation of the Fe hydroxide goethite.

The calculations of Nordstrom (1982) suggest that basaluminite might precipitate first, and, with increasing pH on continued admixing of near-neutral water, gibbsite would become the dominant precipitate. Sampling of the precipitate along traverses of the streams would be required to demonstrate whether such mineral zoning exists. However, one might expect several different aluminous phases to coexist at the same spot, given their sluggish equilibration at the low temperatures of the streams and lakes, as a result of variations in the proportions of acid drainage, near-neutral drainage, and acid-affected snowmelt depending on the time of year.

Are There Even More Strongly Acid Waters Than Those Measured?

The lowest pH values measured by Brown (1993) in his reconnaissance survey of pH in streams, lakes, and seeps was just under 4. We have found mineralogical evidence that <u>may</u> indicate that there are (or were) waters with much lower pH values. The bottom of the valley at the head of the lower F drainage is filled with strongly altered, ochre-colored mud. The stream snaking its way through this marshy area has a pH of about 5. XRD analysis of the mud (AL-6 in Table 1, Fig. 5) yields peaks for opaline silica, alkali feldspar, and a trace of jarosite ($KFe_3(SO_4)_2(OH)_6$). The sandy soil of AL-4, sampled in the F drainage from a steep talus cone at the foot of an area of bedrock that had undergone hydrothermal alteration, proved to be too complex, i.e., have too many phases, to interpret completely, but appears to contain jarosite, alkali feldspar, and

hydrobiotite (mica in which H3O+ replaces K in the mineral structure, due to leaching of the K) (Fig. 6).

The occurrence of jarosite in both samples is signficant because it is generally considered to form under very acid conditions in the weathering environment. For example, Nordstrom (1977) found it precipitating in acid mine drainage with a pH of about 2. During his reconnaissance of the marshy area in the F drainage, Brown (1993) found seeps with pH values just less than 4, but nothing as low as 2. Thermodynamic calculations (Brown 1971) indicate that under the conditions that apply to the study area, i.e., oxidation of pyrite in feldspar- and biotite-rich rocks producing solutions rich in sulfate, iron, and potassium, the stable iron hydroxide is goethite at pH values greater than about 2 and jarosite at lower values. It is possible that in certain places or at certain times of the year the pH is much lower than the values measured, so that jarosite forms. It would then persist, even in contact with water of higher pH, because of the slow kinetics of recrystallization. There is, however, an alternative explanation for the presence of jarosite. It, along with the opaline silica, alkali feldspar and hydrobiotite, may be relict phases eroded from the zones of hydrothermal alteration. The opaline silica and alkali feldspar could be minerals that formed during hydrothermal alteration (and persisted until the present day to due to their great stabilility in the weathering environment), and the jarosite and hydrobiotite could have formed by weathering of the pyrite-bearing hydrothermally altered rocks long ago. For example, there are remnants of extensive mid-Tertiary topographic surfaces preserved in the Sierra Nevada, and the climate at that time was an equitable one that would have favored extensive chemical weathering. It may be that the minerals found in AL-4 and AL-6 are largely relicts from weathering that occurred when the study area was exposed in mid-Tertiary time. Subsequent Holocene (i.e., post-glacial) erosion may have resulted in concentration of these resistant minerals in the present-day soils. In this case, the presence of jarosite has no implications for the acidity of present-day waters.

Geomorphologic Controls on Lake Acidity

The presence of pyrite is a necessary but insufficient condition to generate significant volumes of acid water. Evidence that other factors come into play is the lack of correlation between the exposed mass of pyrite in an area and the

acidity of adjacent lakes. For example, pyrite is extremely abundant in areas near lakes L8, L9, and L10, locally forming massive veins of solid pyrite, yet at the times of the surveys these lakes had pH values greater than 6. In those areas with the lowest pH values, i.e. the acid seeps with pH values just below 4 and lakes with pH values of about 5 in the heads of the C and lower F drainages, pyrite is visible only locally in the hydrothermally altered rocks. An examination of the geomorphology and geology of the C, F, and L drainages reveals that two factors in addition to the presence of pyrite are important in producing acid waters: a continuous supply of water and a process that reduces grain size of rocks (Fig. 7).

There must be a continuous supply of water in contact with the pyrite in order to produce acid and then transport it into adjacent bodies of water. The large area of hydrothermal alteration south of L7 lies on a talus-covered slope; flushing by rainwater and snowmelt, as well as groundwater flow, probably accounts for its acid contribution to L7. The absence of such a supply of water is why several of the lakes adjacent to strong pyritization in the L drainage are not strongly acid. The area of pyritization near L9 and L10 is a small ridge within an open basin, so no surface water runs over it to contribute acid water to these lakes. Lack of water to mobilize acid may also explain why the patch of pyritization near N3 and O26 does not contribute acidity to those lakes. The presence of a rock glacier at the south end of the C drainage provides a year-round supply of water to react with the hydrothermally altered rocks it contains, as the icy matrix melts during the summer (Fig. 7). Steep, north-facing slopes at high elevations (e.g., at the heads of the B, C, D and F drainages) that sustain glaciers or (in years other than the past drought years) perennial snow provide a year-round source of meltwater.

We also speculate that the constant presence of water may also be important because it supports a variety of bacilli and algae, which may catalyze the oxidation of pyrite. One type of acidophillic bacilli, the genus Thiobacillus, is known to be a catalyst to the oxidation of pyrite by way of its rapid oxidation of sulfur and ferrous iron (Singer and Stumm, 1970). Microbial catalysis speeds the rate-limiting step of pyrite breakdown (the transformation of ferrous iron in solution to ferric iron, which can then act as an oxidant for pyrite to produce sulfuric acid) by orders of magnitude over abiotic conditions. In the absence of water and microbial activity, the rate of pyrite breakdown is limited by the slow rate of oxygen diffusion through

reaction products on the mineral surface. If pyrite-bearing rocks remain dry most of the time, they may produce rather little acid because thiobacilli would have no access and pyrite breakdown would eventually halt when the development of a thin rind of breakdown products on the pyrite grains inhibited oxygen diffusion to the reaction front. To determine whether this hypothesis has any validity would require analyses of acid waters for acidophilllic bacilli.

Increasing reaction rates by increasing the surface of fresh pyrite exposed to the atmosphere or water may also be important in producing significant amounts of acid water. We speculate that this may be especially important when the total amount of pyrite is not large, as it is in the study area, compared to many mining districts in which acid mine drainage is a problem. By increasing the surface area of pyrite, it may result in a greater amount of acidification. We hypothesize that reduction in grain size of the rock is important in producing acid waters because the lowest measured pH values--in lake C24 and in the marsh at the head of the lower F drainage--are found in bodies of water adjacent to two different geologic features that result in crushing of hydrothermally altered rock.

The first geologic agent of grain reduction is the rock glacier at the head of the C drainage (Fig. 1). Rock glaciers--mixtures of rock and ice that occur on north-facing cirque headwalls--flow downhill and in the process scour their bedrock and crush rocks contained within it. In the case of the rock glacier above lake C24, the bedrock and most of the entrained blocks consist of hydrothermally altered metasedimentary rocks. Thus the rock glacier provides both the water and newly fractured surfaces of pyrite for it to react with (Fig. 7). The second geologic feature is the fault in the F drainage (Fig. 1). Although there is no evidence that this fault is presently active, movement along it in the past has resulted in the rocks within the fault zone being ground up and pulverized. This has also made them easy to erode, probably accounting in part for the large amount of surficial material at the head of the lower F drainage (Fig. 7).

Speculations Concerning the Impact of Anthropogenic Acidity on the Study Area

Near the beginning of this report we dismissed acid precipitation as the main cause of lake acidity because it cannot account for the large range of pH values in small areas. However, the presence of acid precipitation in the Emerald Lake basin and even in Mammoth, which is much farther from sources of smog,

suggests that the study area is indeed impacted by acid rain and snow. A future interpretation of the water analyses being done by Aaron Brown might allow an estimate of the amount of sulfate contributed by acid precipitation and therefore the acidity that has been neutralized through water-rock reactions. In the absence of additional sources of acidity like pyrite, the importance of geology would be in determining the acid-neutralizing capacity afforded by bedrocks of different types. There is preliminary evidence for such control in the existing pH measurements. The highest pH measurements (in lakes of sufficient size to insure that they were not affected by evaporation or biological activity) were found in lakes O13 and O8, which our reconnaissance mapping shows are the only lakes measured during the surveys that lie in watersheds containing significant amounts of marble (Fig. 1). This observation leads us to hypothesize that all lakes in the study area are affected by acid precipitation, and that it is fully neutralized only in the eastern O drainage where highly reactive rocks with a large neutralizing capacity--marbles--are found.

A number of workers have emphasized the susceptibility of Sierran alpine lakes to the effects of anthropogenic sources of acid rain due to their dilute nature and low acid-neutralizing capacity. The low acid-neutralizing capacity is a result of the bedrock for most of the Sierra being weakly reactive granitic rocks with a high proportion of feldspar and quartz and low proportions of Ca, Fe-, and Mg-rich phases, which yield more H+ on weathering. We suggest, however, that it may not be accurate to make predictions concerning the fate of Sierran alpine lakes receiving acid precipitation based on the more extensively studied lakes in similar granitic terrains in eastern North America or Scandinavia because the geomorphologic settings are so different. The Sierra has the steep topography and high elevations of an area characterized by alpine glaciation, whereas the northeastern U.S. and Scandinavia are areas of low relief at relatively low elevations that were covered by continental ice sheets. The vigor of mechanical weathering imposed by diurnal freezing and thawing of water in the high-elevation Mt. Pinchot region, combined with steep slopes produced by alpine glaciation, results in many lakes being bordered entirely or partially by talus slopes or piles of rock fall (Fig. 7). Earthquakes in the region activate talus slopes and cause new rock falls, as does freeze-thaw cycling of the strongly jointed cliffs; thus the lake waters come into contact with fresh, reactive rock surfaces. In contrast, lakes in the tectonically quiet northeastern U.S. or Scandinavia either

occupy low, scooped basins. or, more commonly, hollows in deeply weathered glacial debris. The result is that the surface area of rock exposed to lake water is less and the lake water does not come into contact with fresh rock surfaces. This means that once the rocks and deposits in the lakebed have reacted with water affected by acid precipitation to neutralize it, further acid-neutralization is inhibited by the presence of weathering reaction products. On the other hand, the acid-neutralizing capacity of Sierran lakes is constantly being renewed by the exposure of new fresh rock surfaces. The difference in topographic and tectonic setting may make Sierran lakes somewhat more resilient in responding to acid precipitation than lakes in identical rocks in areas that underwent continental glaciation.

ACKNOWLEDGMENTS

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Table 1. Results of Analyses of Precipitates

Sample #	Locality	Description	Composition[1]
AL-1	stream between C22 and C21	grey-white coating on granite	Al>S>Si
AL-2	stream between F2 and F1	grey-white coating on granite	Al>Si=S
AL-3	" "	pinkish-white coating on granite	Al>S>Si>Fe
AL-8c	shore of O13, an alkaline lake	black coating on schist	Ca>Fe>Al>K>Si
AL-11	White Fork, east of L8, at confluence with major, neutral stream from N	grey-white coating on schist	Al>S>Si>Fe

[1]Oxygen and water are assumed present.

Figure 1. Simplified geologic map of Mt. Pinchot study area, based on mapping by Moore (1963), showing labels for drainage basins and lakes.

Figure 2. X-ray diffraction pattern for white precipitate in stream in F drainage, showing that it is amorphous.

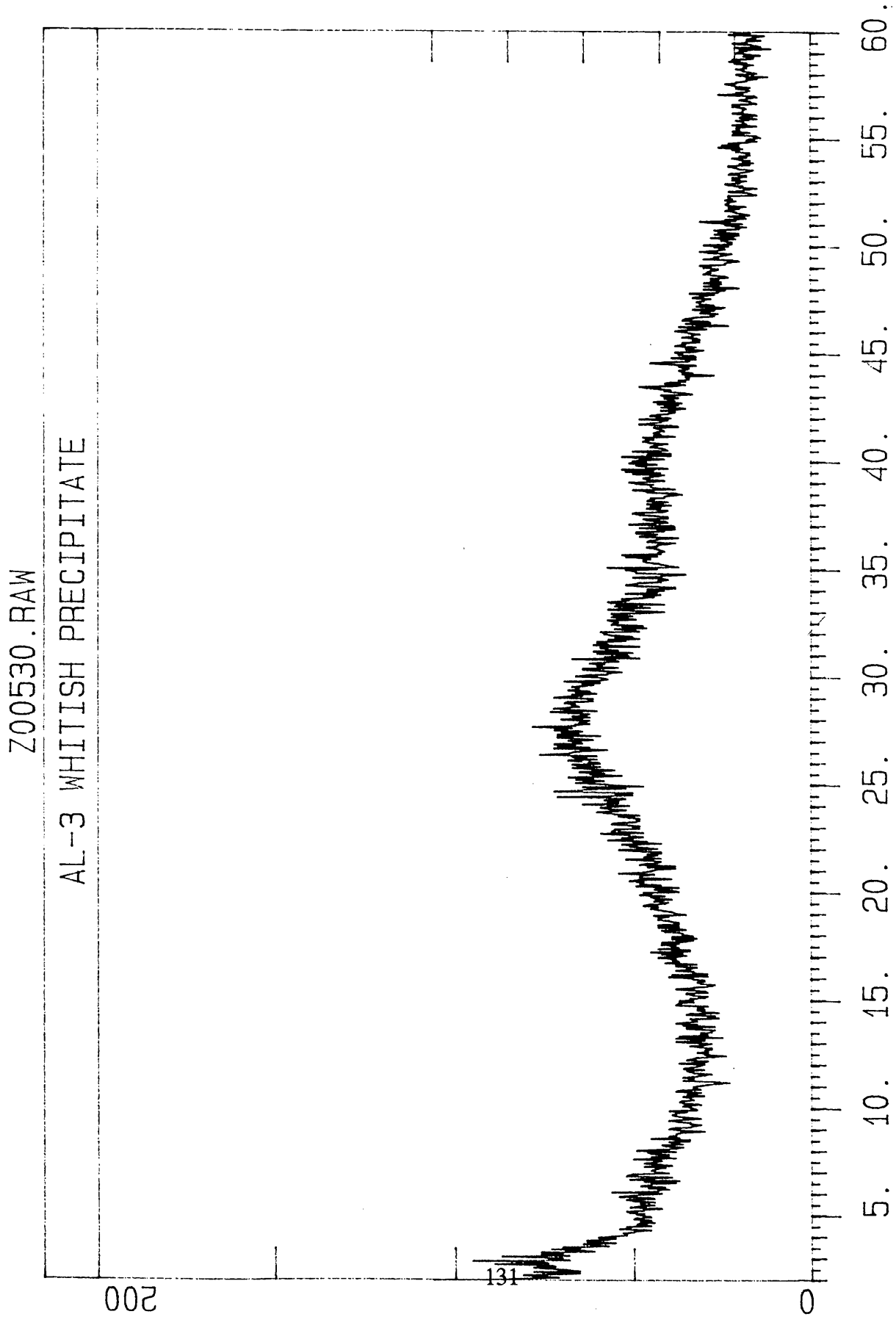
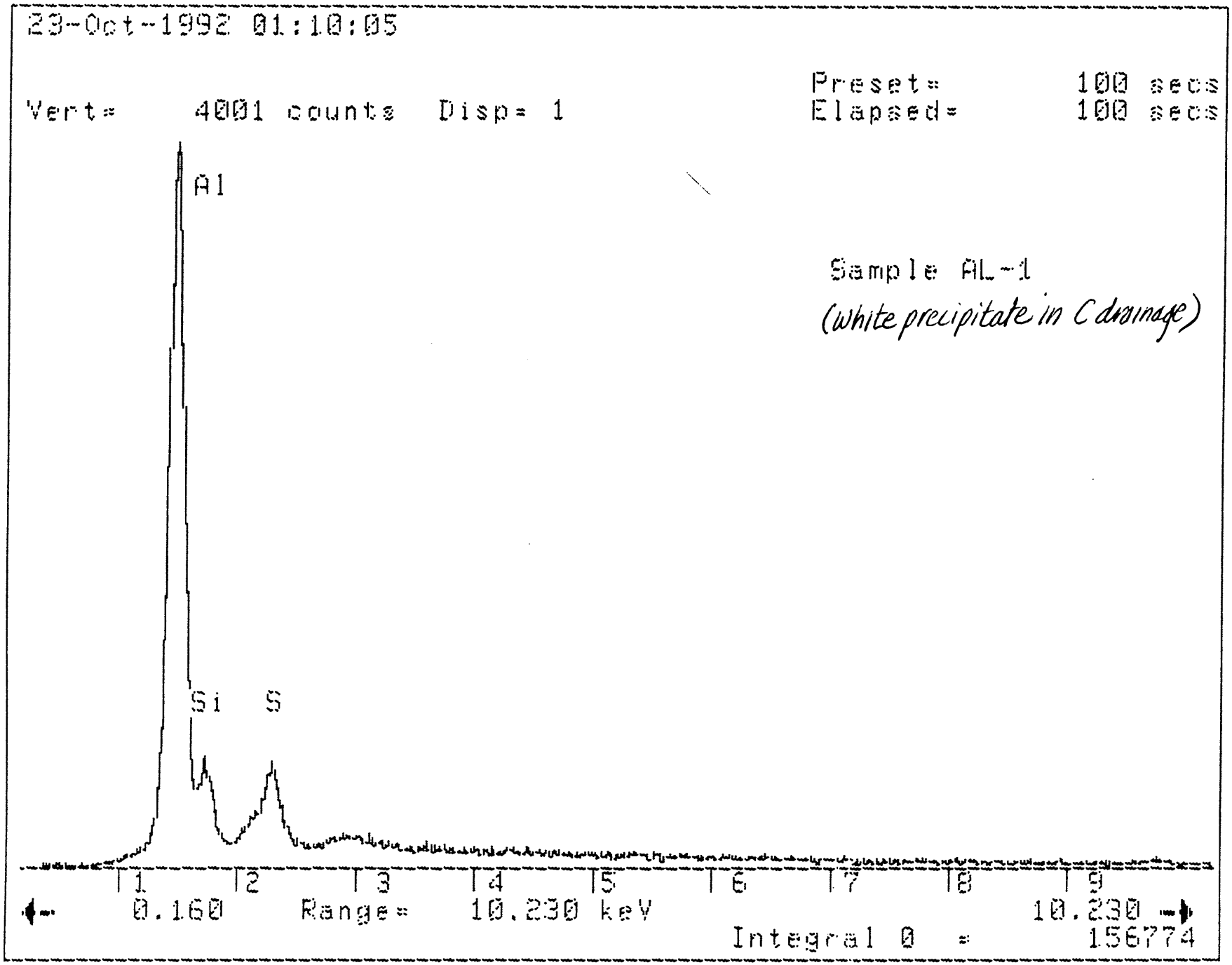
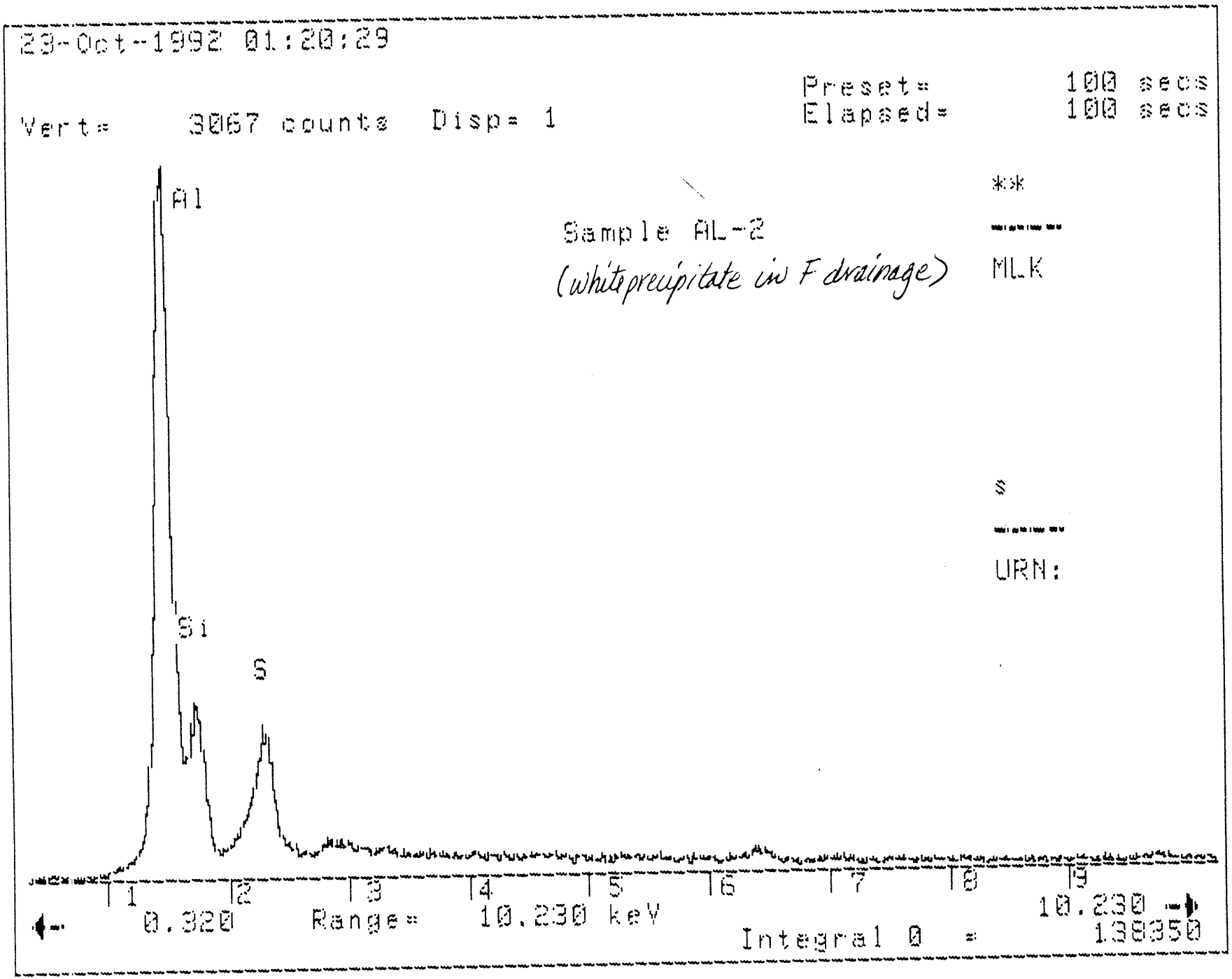
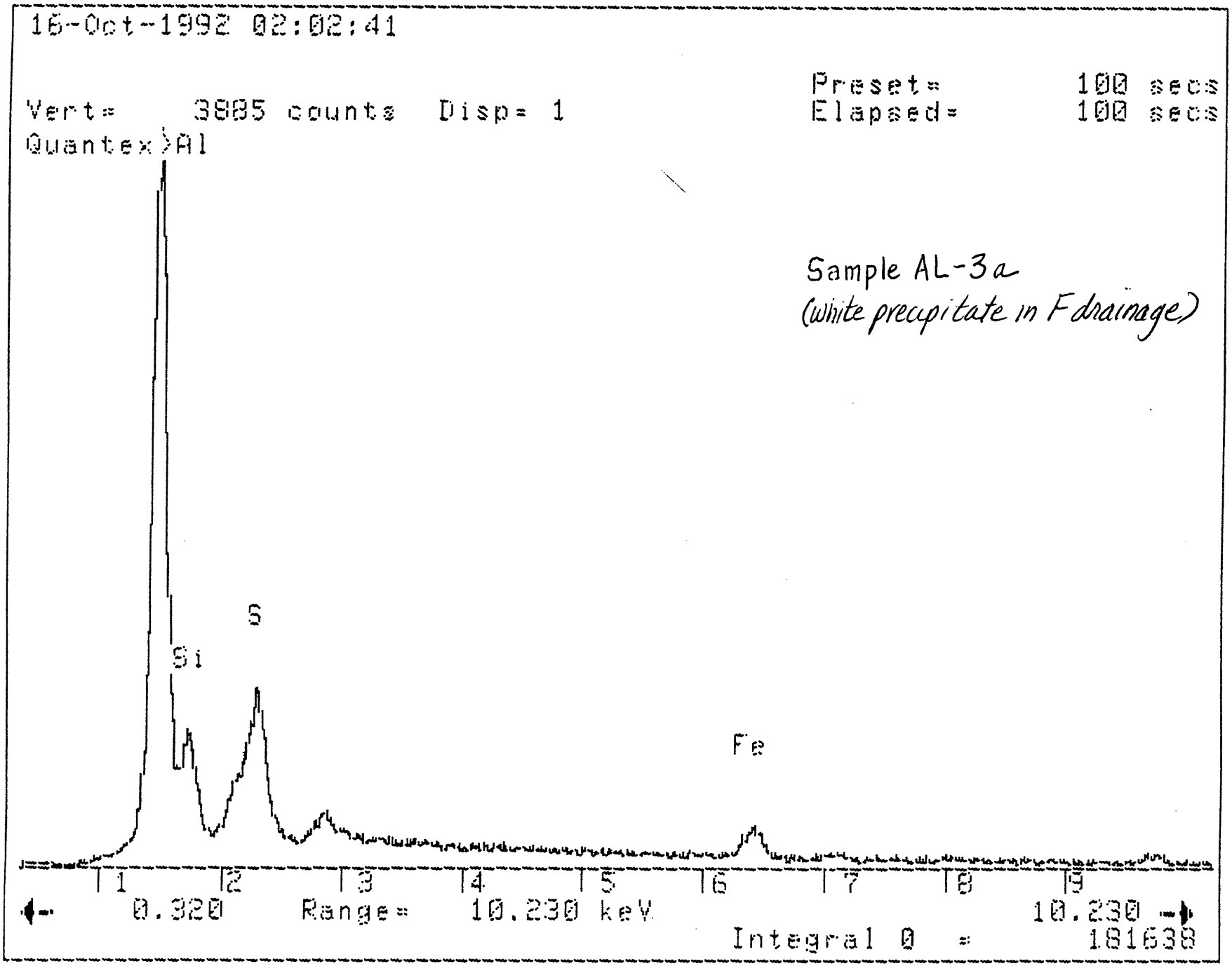
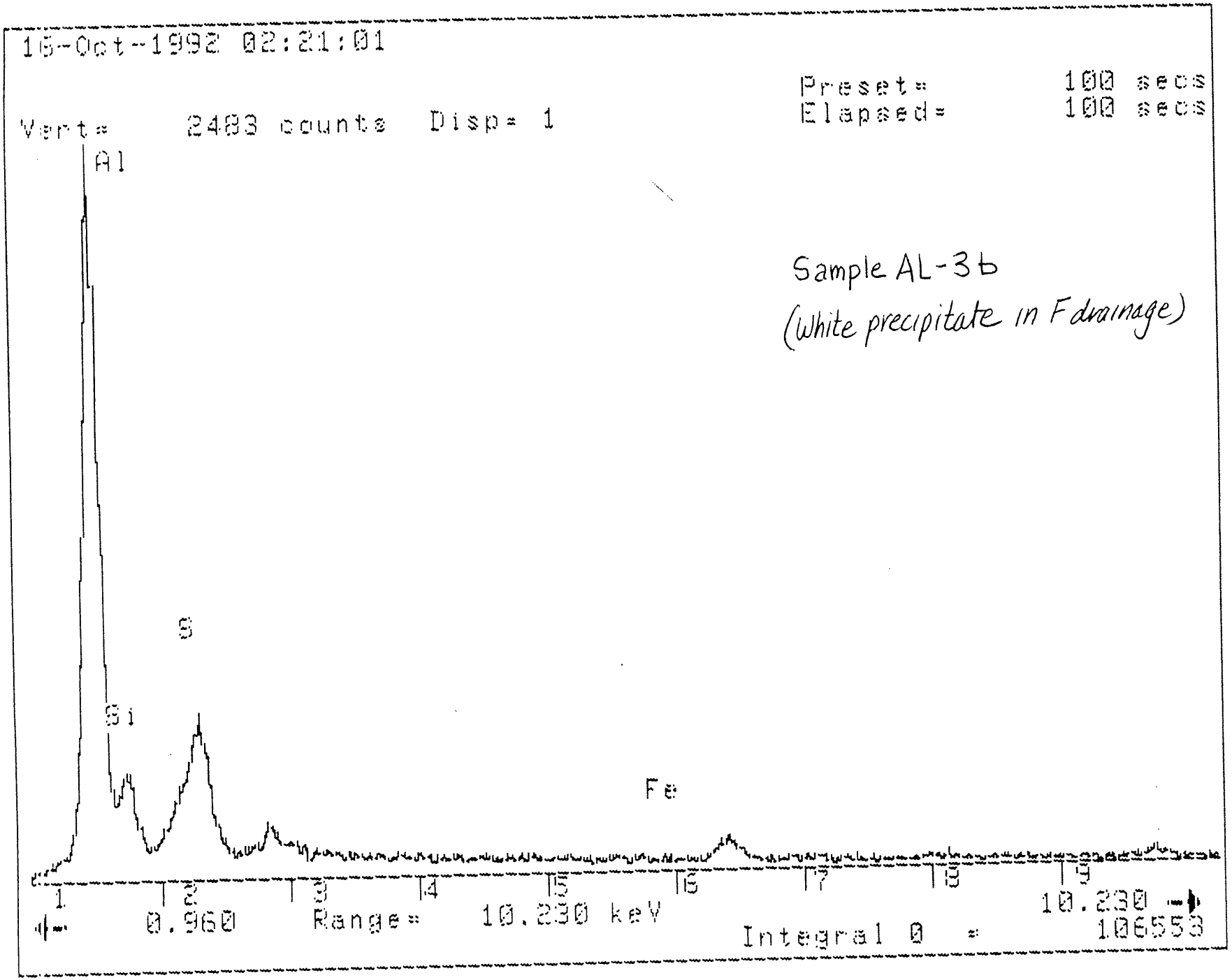


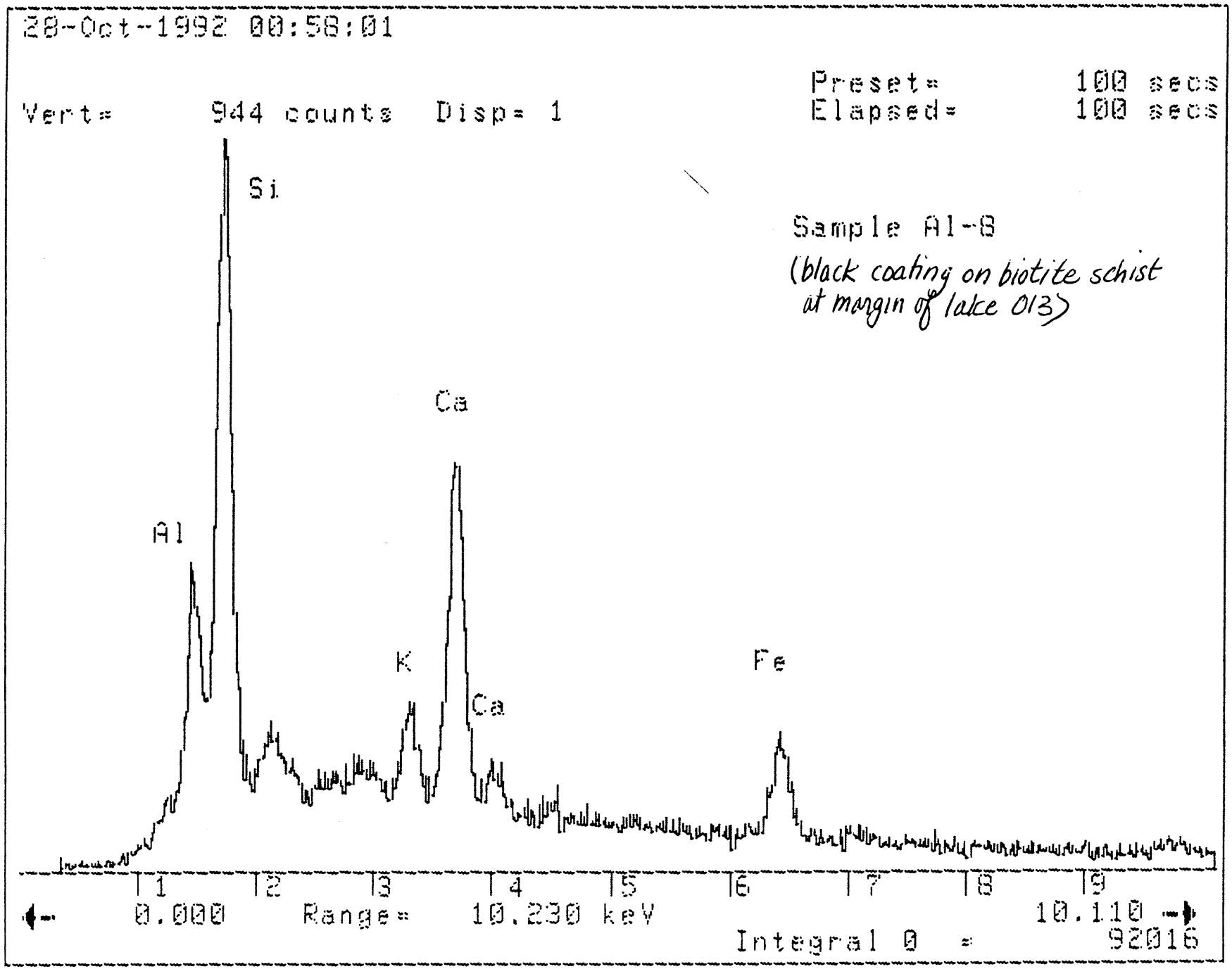
Figure 3. Energy-dispersive analyses of white precipitates in streambeds of C, F, and L drainages, black coating on rocks at lake O13, and fresh rock surfaces for comparison. The white precipitates show peaks for Al, Si, S, ± Fe, indicating they consist mostly of a hydrated aluminous sulfate compound, locally with a trace of iron hydroxide.

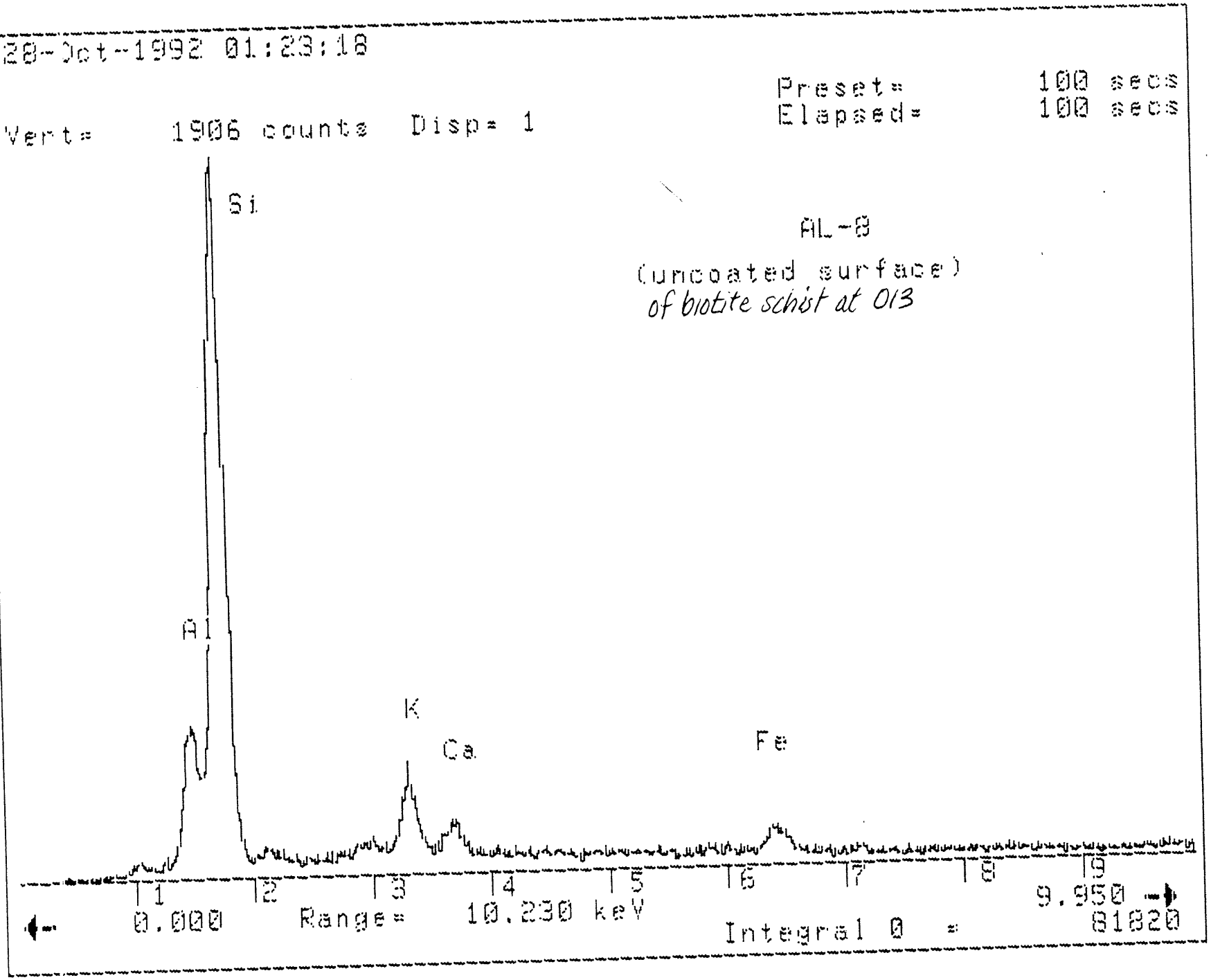

23-Oct-1992 01:10:05
Vert= 4001 counts Disp= 1
Preset= 100 secs
Elapsed= 100 secs
Al
Si
S
Sample AL-1
(white precipitate in C drainage)
1
2
3
4
5
6
7
8
9
0.160
Range= 10.230 keV
10.230
Integral 0 = 156774

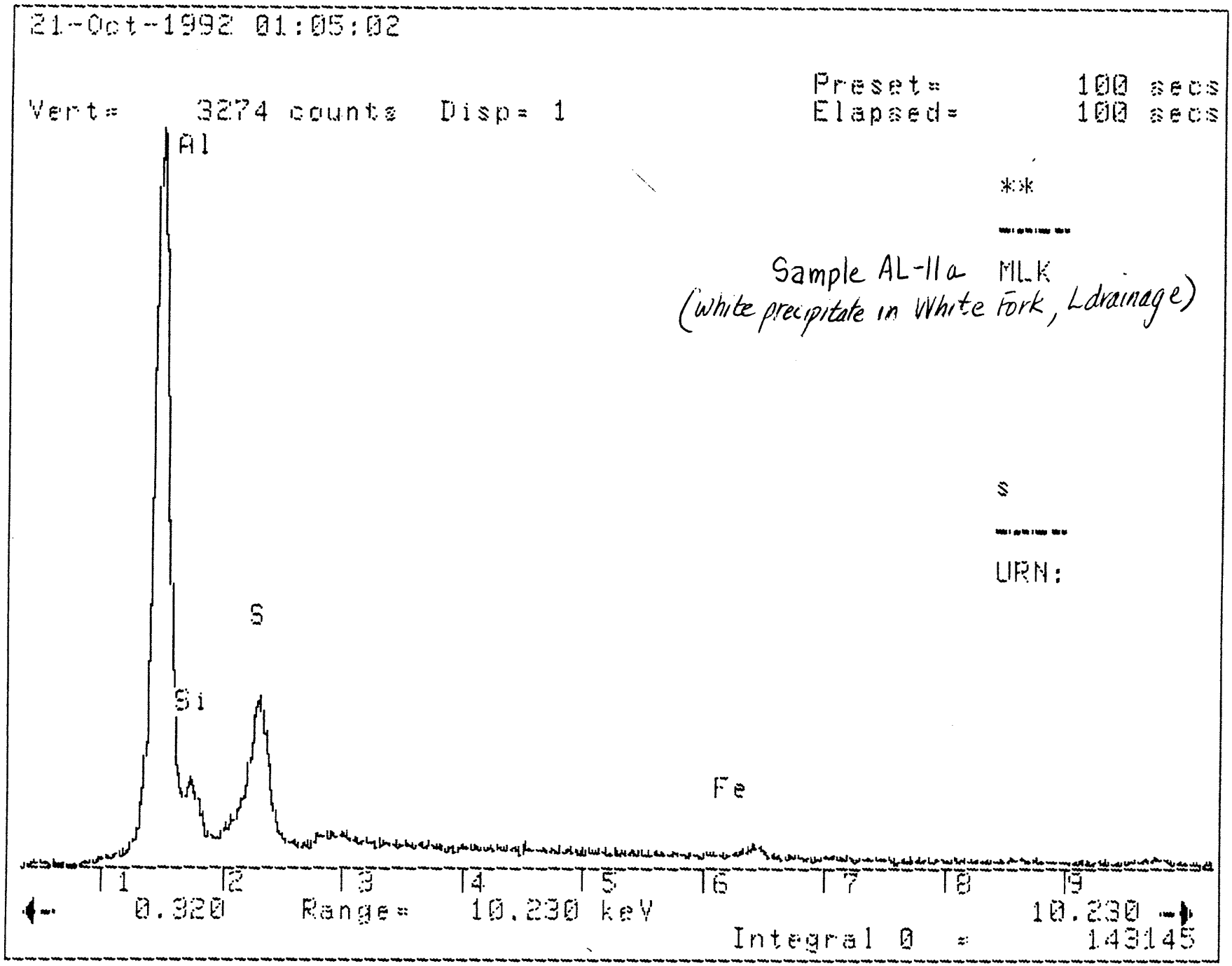

23-Oct-1992 01:20:29
Preset= 100 secs
Elapsed= 100 secs
Vert= 3067 counts Disp= 1
Al
Si
S
Sample AL-2
(white precipitate in F drainage)
**
MLK
$
URN:
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 138350

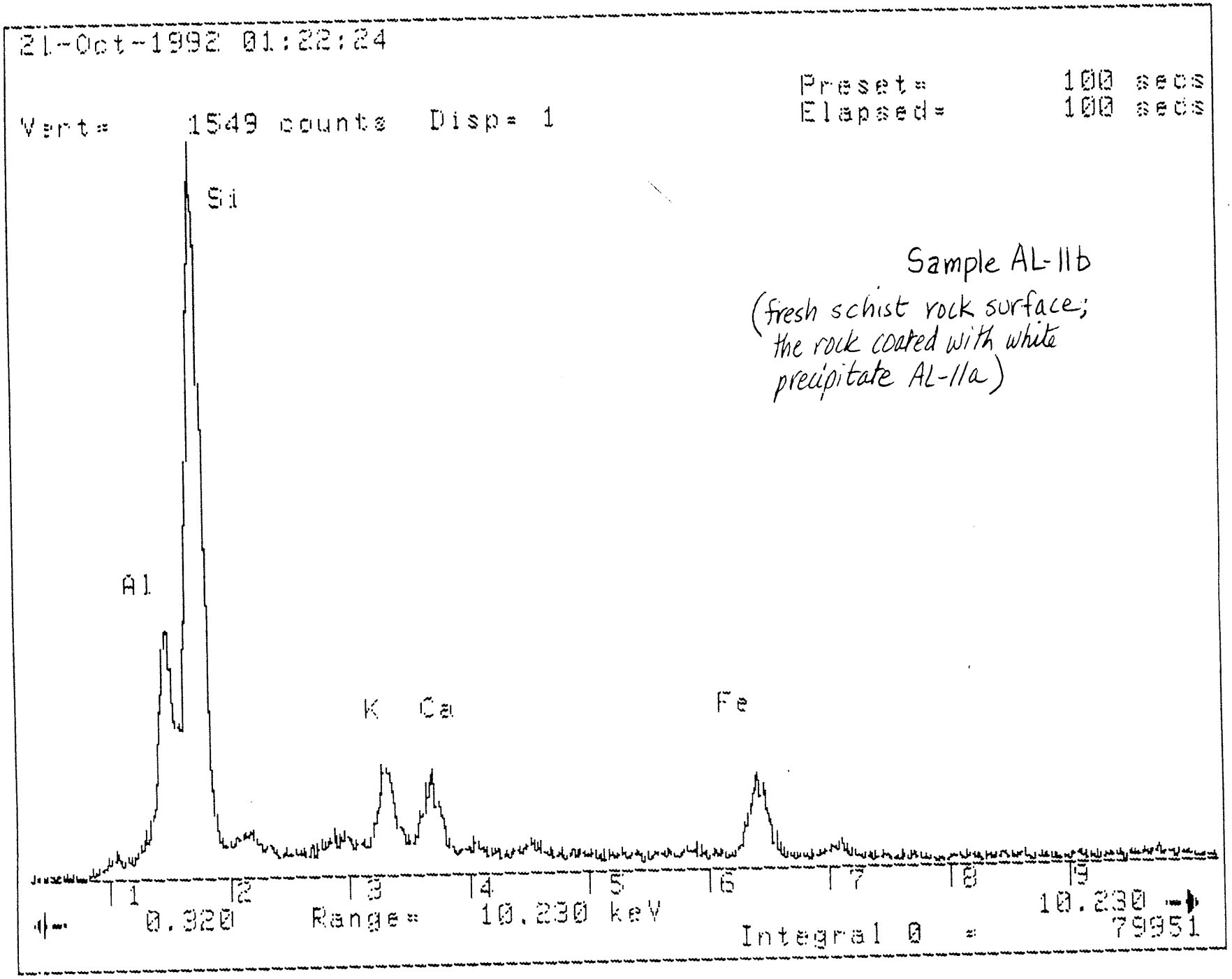

16-Oct-1992 02:02:41
Preset= 100 secs
Vert= 3885 counts Disp= 1
Elapsed= 100 secs
Quantex>Al
Sample AL-3a
(white precipitate in F drainage)
Si
S
Fe
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 181638

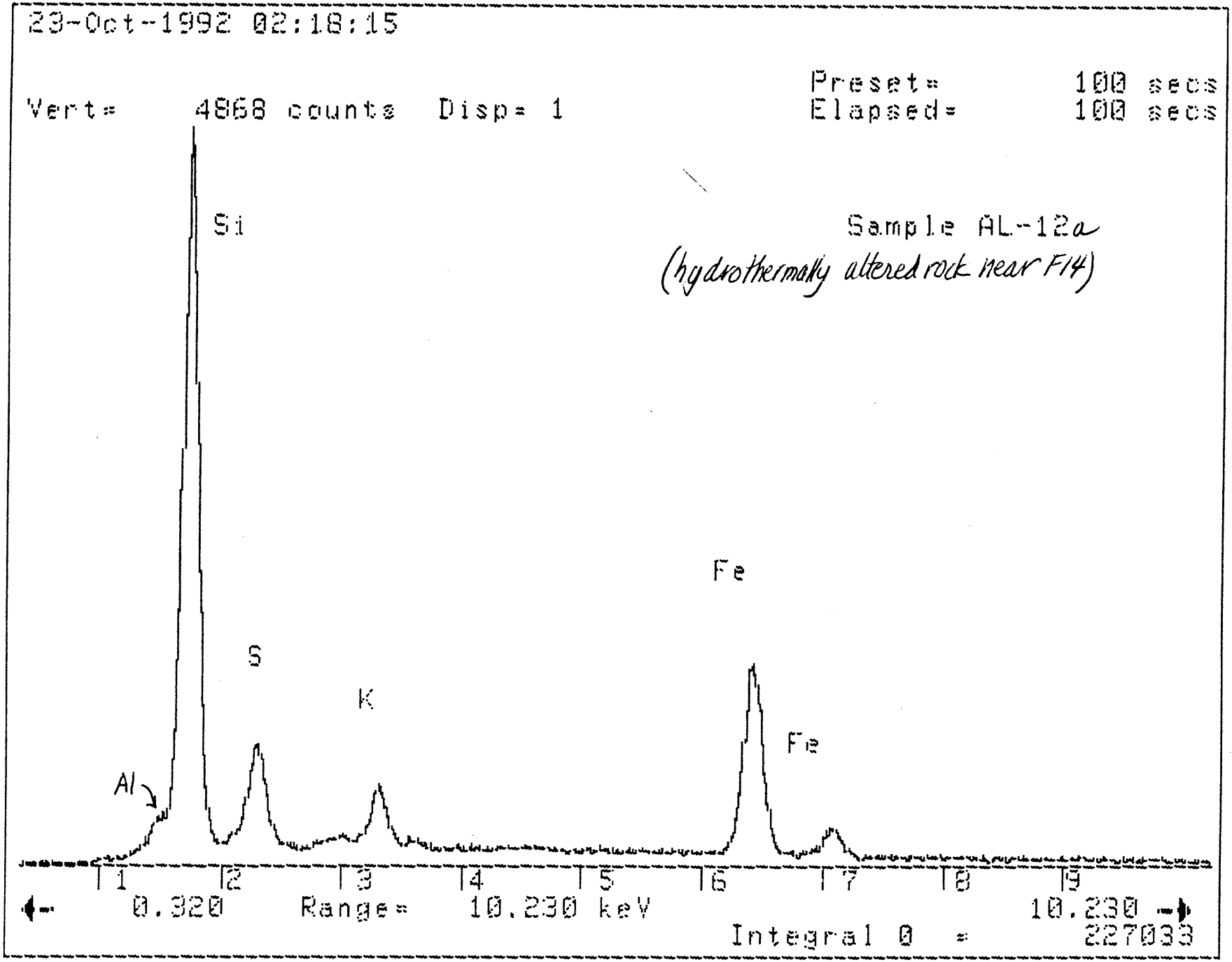

16-Oct-1992 02:21:01
Preset= 100 secs
Elapsed= 100 secs
Vert= 2483 counts Disp= 1
Al
Si
S
Fe
Sample AL-3b
(White precipitate in F drainage)
1
2
3
4
5
6
7
8
9
0.960
Range= 10.230 keV
10.230
Integral 0 = 106553

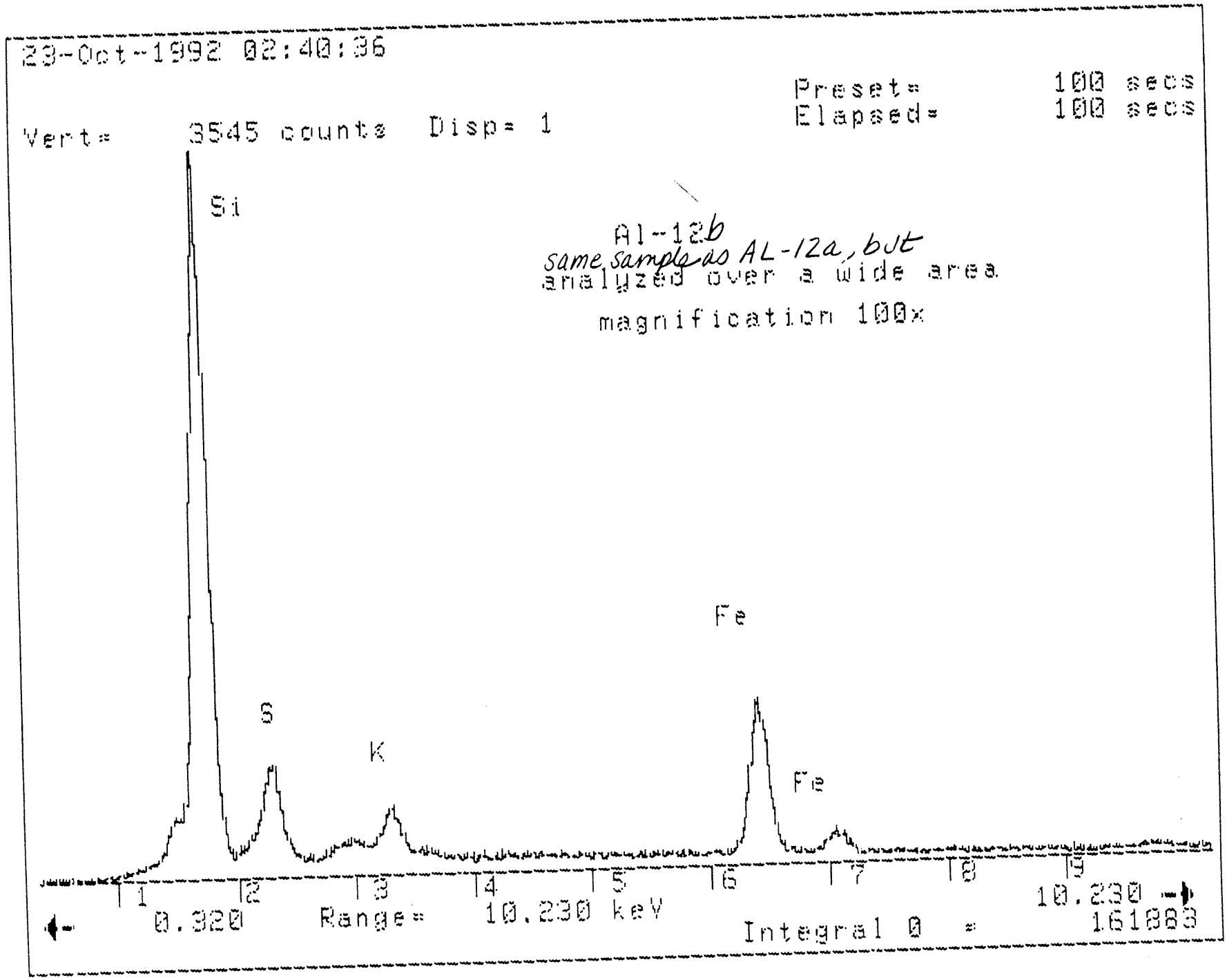

28-Oct-1992 00:58:01
Preset= 100 secs
Elapsed= 100 secs
Vert= 944 counts Disp= 1
Sample A1-B
(black coating on biotite schist at margin of lake 013)
Si
Al
Ca
K
Ca
Fe
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.110
Integral 0 = 92016


20-Oct-1992 01:23:18
Preset= 100 secs
Elapsed= 100 secs
Vert= 1906 counts Disp= 1
Si
Al
K
Ca
Fe
AL-B
(uncoated surface)
of biotite schist at 013
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
9.950
Integral 0 = 81820


21-Oct-1992 01:05:02
Preset= 100 secs
Elapsed= 100 secs
Vert= 3274 counts Disp= 1
Al
Si
S
Fe
**
Sample AL-11a MLK
(White precipitate in White Fork, Ldrainage)
S
URN:
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 143145


21-Oct-1992 01:22:24
Preset= 100 secs
Elapsed= 100 secs
Vert= 1549 counts Disp= 1
Si
Al
K Ca
Fe
Sample AL-11b
(fresh schist rock surface; the rock coated with white precipitate AL-11a)
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 79951


23-Oct-1992 02:18:15
Vert= 4868 counts Disp= 1
Preset= 100 secs
Elapsed= 100 secs
Sample AL-12a
(hydrothermally altered rock near F14)
Si
S
K
Al
Fe
Fe
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 227033


23-Oct-1992 02:40:36
Preset= 100 secs
Elapsed= 100 secs
Vert= 3545 counts Disp= 1
Si
Al-12b
same sample as AL-12a, but
analyzed over a wide area.
magnification 100x
S
K
Fe
Fe
1
2
3
4
5
6
7
8
9
0.320
Range= 10.230 keV
10.230
Integral 0 = 1610883

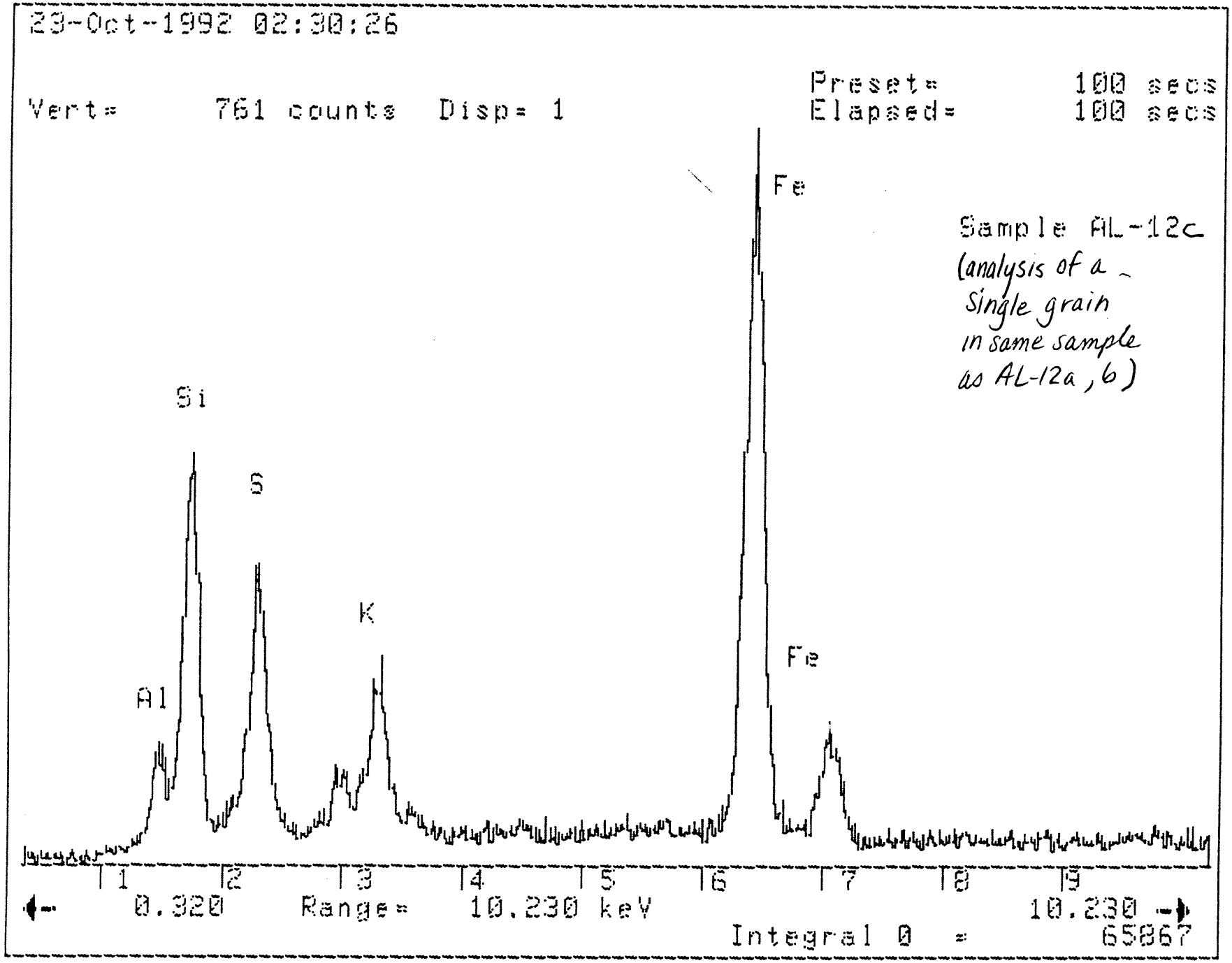

23-Oct-1992 02:30:26
Vert= 761 counts Disp= 1
Preset= 100 secs
Elapsed= 100 secs
Fe
Sample AL-12c
(analysis of a
single grain
in same sample
as AL-12a, b)
Si
S
K
Al
Fe
1
2
3
4
5
6
7
8
9
0.920
Range= 10.230 keV
10.230
Integral 0 = 65867

Figure 4. Solubility curves for various hydrated aluminous minerals as a function of pH (from Nordstrom (1982, Fig. 5), assuming a potassium activity of 10-4 M, for conditions applicable to (a) acid rain and (b) acid mine drainage.

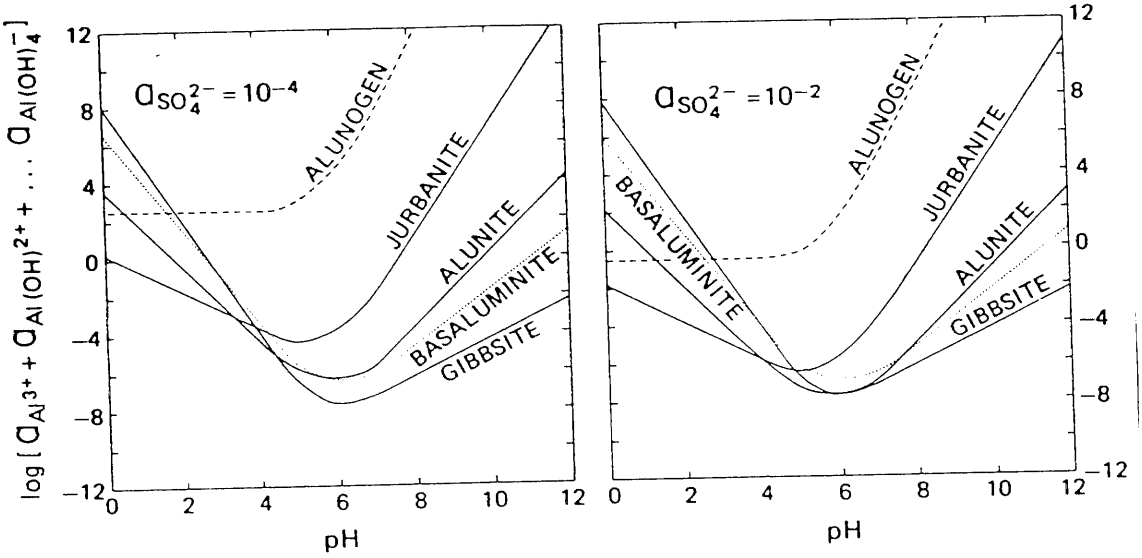


Figure 5. X-ray diffraction pattern for ochre-colored mud (sample AL-6) in the marshy area near the head of lower F drainage.

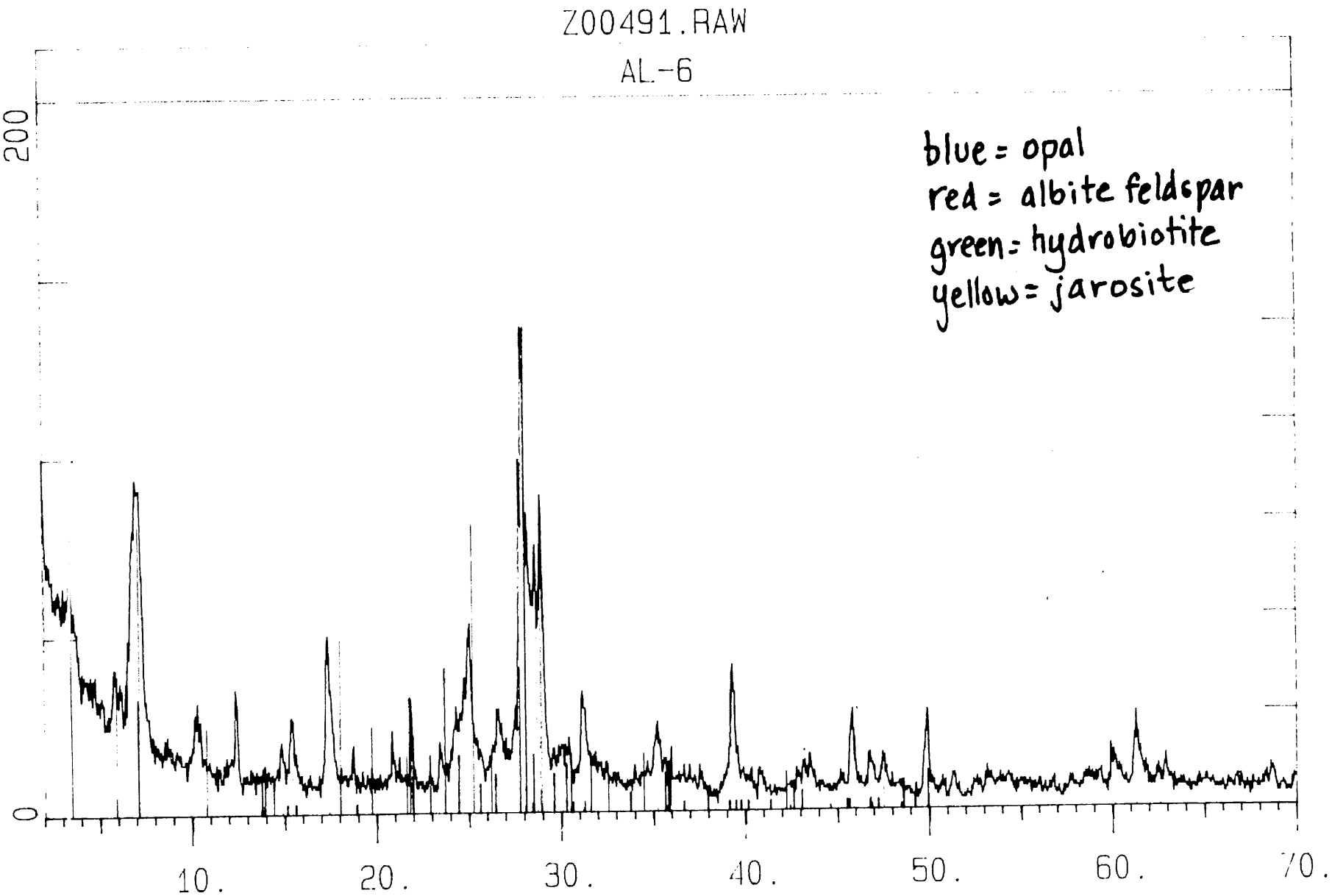

Z00491.RAW
AL-6
200
0
10.
20.
30.
40.
50.
60.
70.
blue = opal
red = albite feldspar
green = hydrobiotite
yellow = jarosite

Figure 6. X-ray diffraction pattern for yellow soil (sample AL-4) in talus slope at foot of cliff containing hydrothermally altered metamorphic rocks at the head of lower F drainage.

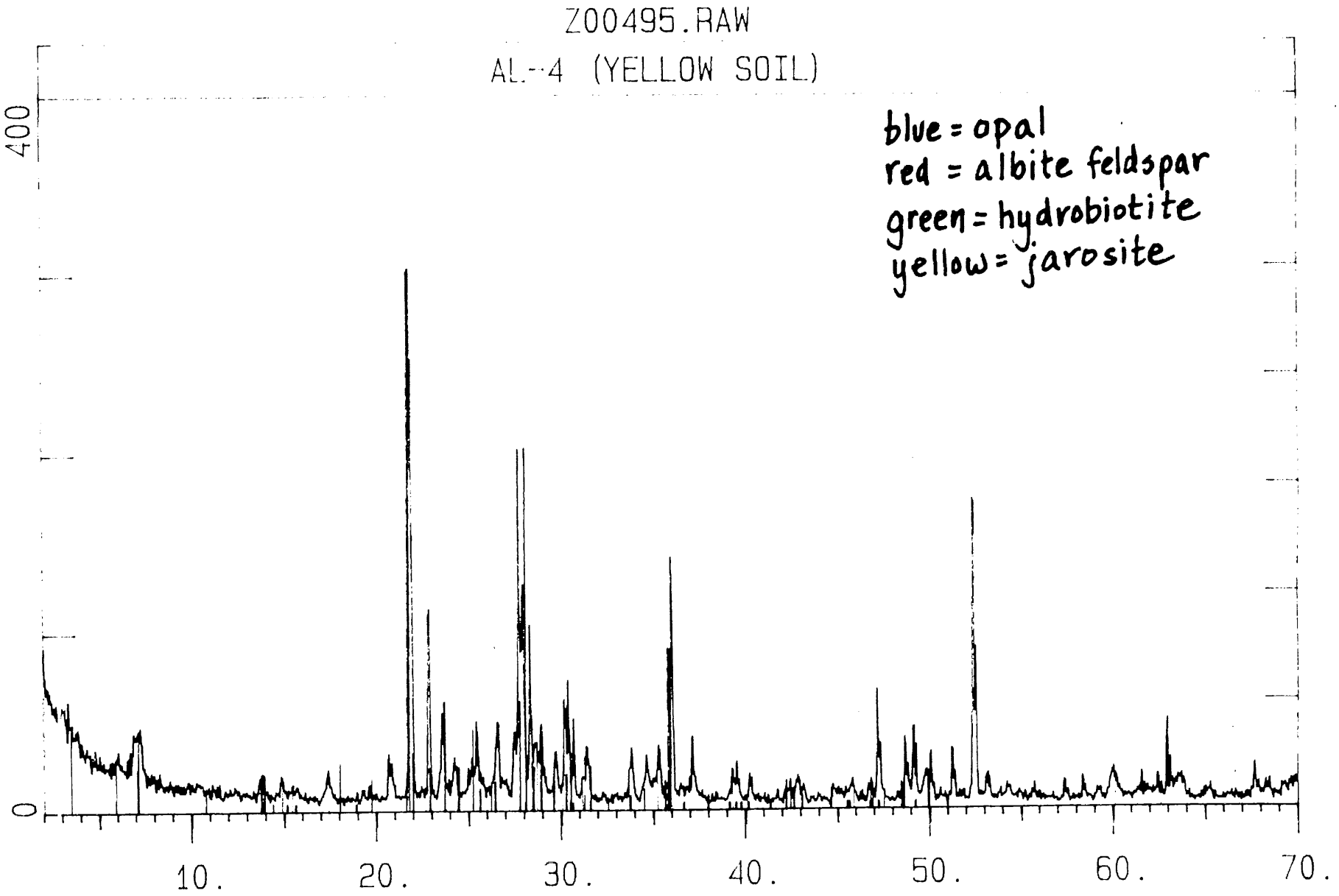
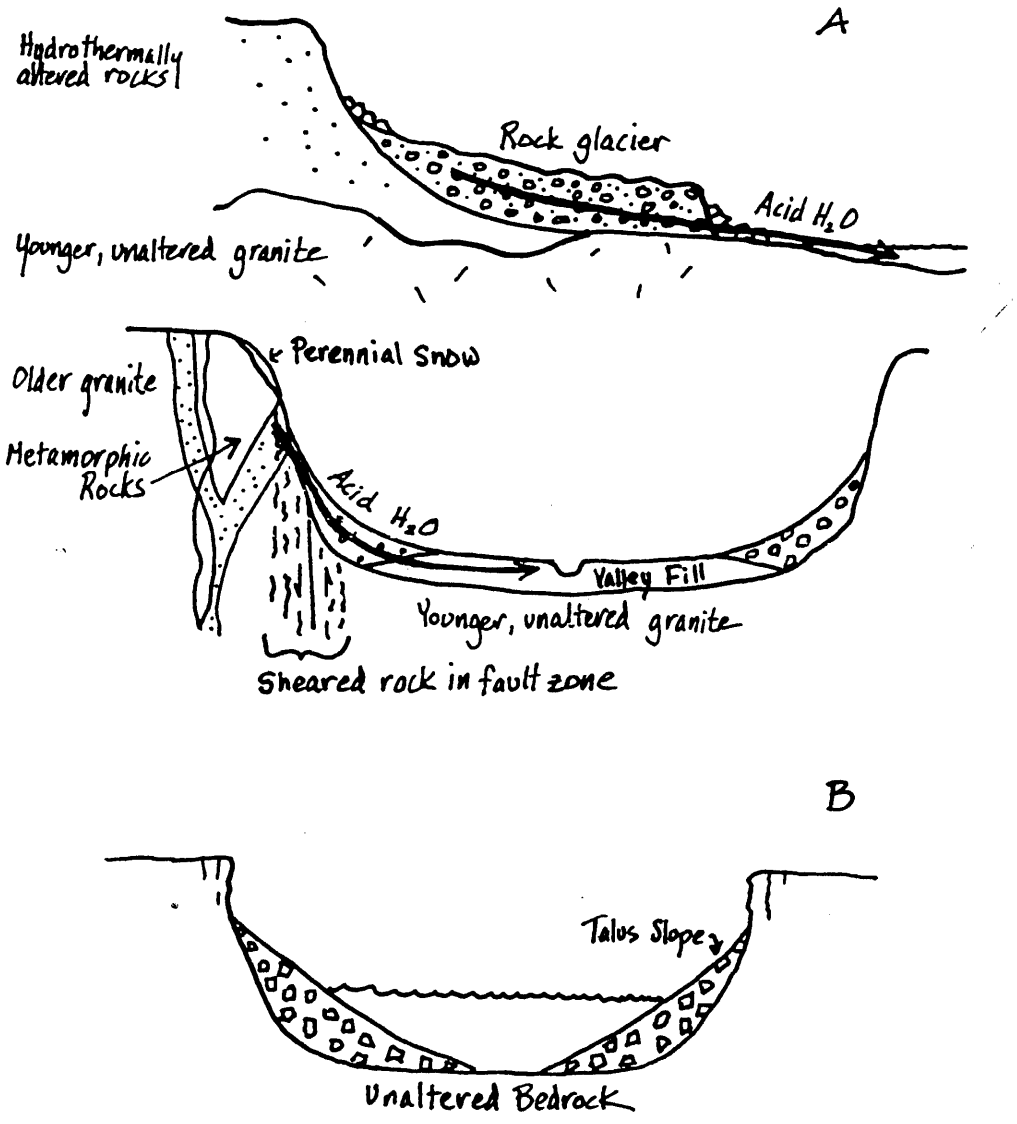
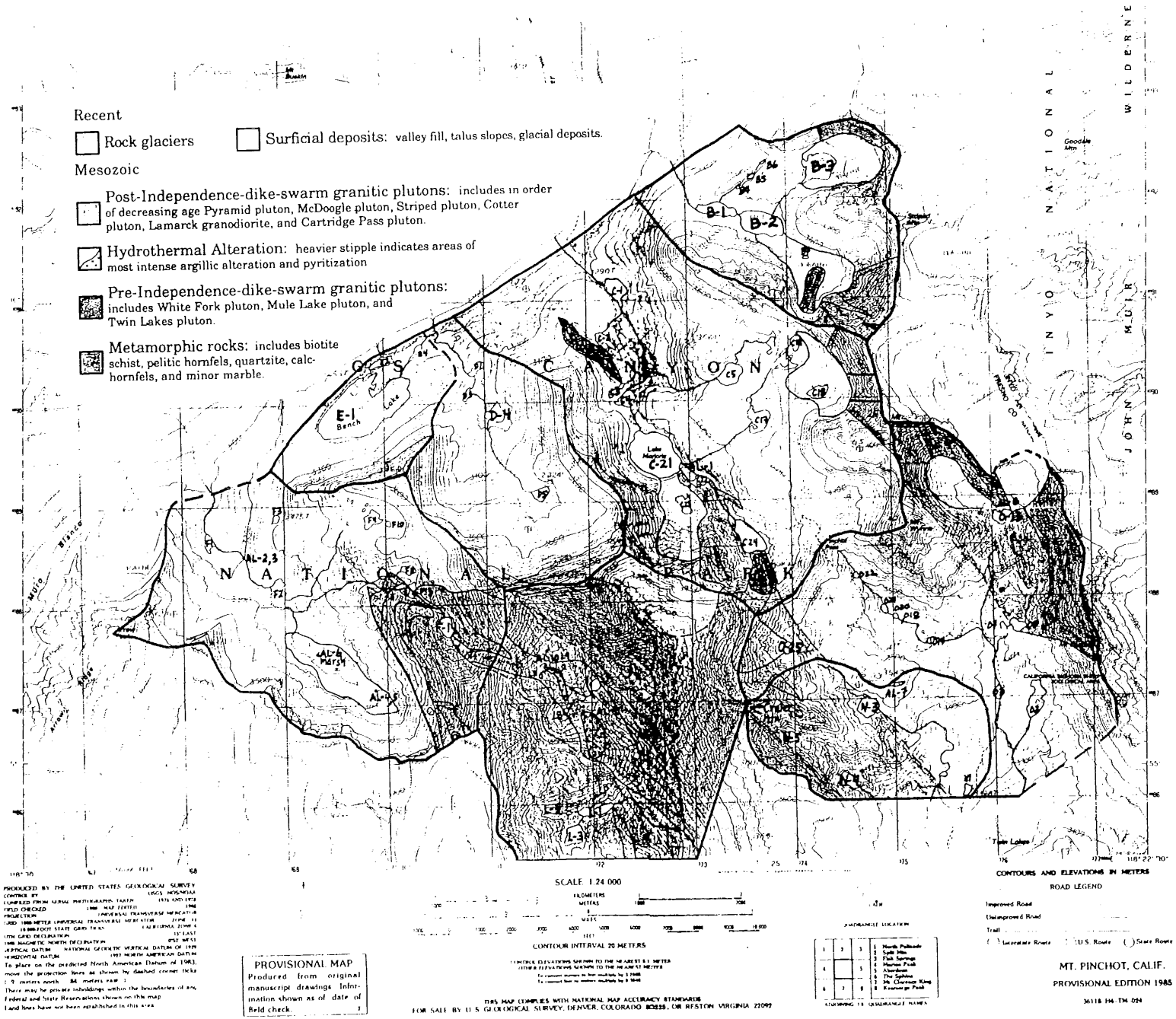
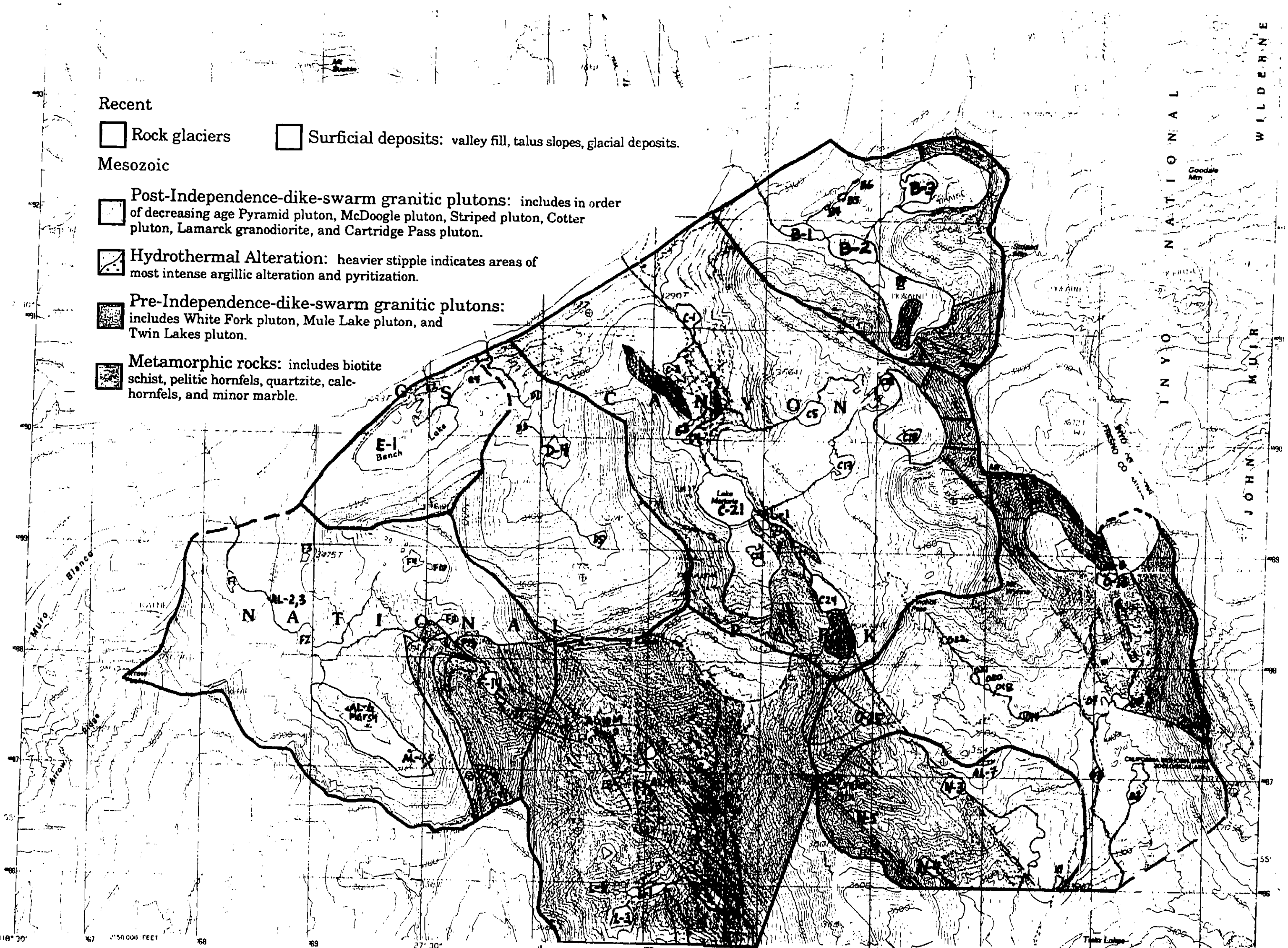

Z00495.RAW
AL--4 (YELLOW SOIL)
400
0
10.
20.
30.
40.
50.
60.
70.
blue = opal
red = albite feldspar
green = hydrobiotite
yellow = jarosite

Figure 7. Schematic diagrams illustrating models for acidified and neutral lakes. (A) "Espresso" acid lakes: The rock glacier grinds pyrite-bearing rocks, increasing surface area for acid-producing weathering reactions, and, at the same time, provides a continuous source of water from Spring to Fall to express the acid water so produced. This corresponds to the conditions for Lake C24. Alternatively, grain size reduction of pyrite-bearing rocks in a fault zone also yields acid water, which due to the steep topography imposed by the fault itself, is not diluted by drainage from a broad area. This corresponds to conditions for the marshy area at the head of lower F drainage. (B) "Teabag" lakes: These are generally cirque lakes with shores consisting mostly of talus slopes or cliffs footed by rock fall. The blocks of unweathered rock "steep" in lake water; acid-neutralizing reactions occur on the freshly broken sufaces, leading to neutral lake water or moderating the pH of lakes that otherwise would have been acid. Examples in the study area are C23 (in granodiorite) and O13 (in calc-silicate and carbonate rocks).




Recent
Rock glaciers
Surficial deposits: valley fill, talus slopes, glacial deposits.
Mesozoic
Post-Independence-dike-swarm granitic plutons: includes in order of decreasing age Pyramid pluton, McDoogle pluton, Striped pluton, Cotter pluton, Lamarck granodiorite, and Cartridge Pass pluton.
Hydrothermal Alteration: heavier stipple indicates areas of most intense argillic alteration and pyritization
Pre-Independence-dike-swarm granitic plutons: includes White Fork pluton, Mule Lake pluton, and Twin Lakes pluton.
Metamorphic rocks: includes biotite schist, pelitic hornfels, quartzite, calc-hornfels, and minor marble.
INYO NATIONAL WILDERNESS
JOHN MUIR
SCALE 1:24 000
CONTOUR INTERVAL 20 METERS
CONTOURS AND ELEVATIONS IN METERS
ROAD LEGEND
Improved Road
Unimproved Road
Trail
PROVISIONAL MAP
Produced from original manuscript drawings. Information shown as of date of field check.
MT. PINCHOT, CALIF.
PROVISIONAL EDITION 1985



PRODUCED BY THE UNITED STATES GEOLOGICAL SURVEY
CONTROL BY ... USGS, NOS/NOAA
COMPILED FROM AERIAL PHOTOGRAPHS TAKEN 1976 AND 1978
FIELD CHECKED 1980 MAP EDITED 1985
PROJECTION ... UNIVERSAL TRANSVERSE MERCATOR
GRID: 1000-METER UNIVERSAL TRANSVERSE MERCATOR ZONE 11
10,000-FOOT STATE GRID TICKS CALIFORNIA, ZONE 4
UTM GRID DECLINATION ... 1½° EAST
1980 MAGNETIC NORTH DECLINATION ... 0°52' WEST
VERTICAL DATUM ... NATIONAL GEODETIC VERTICAL DATUM OF 1929
HORIZONTAL DATUM ... 1927 NORTH AMERICAN DATUM

To place on the predicted North American Datum of 1983, move the projection lines as shown by dashed corner ticks (9 meters north 84 meters east)

There may be private inholdings within the boundaries of any Federal and State Reservations shown on this map

Land lines have not been established in this area

PROVISIONAL MAP
Produced from original manuscript drawings. Information shown as of date of field check.

SCALE 1:24 000

CONTOUR INTERVAL 20 METERS

CONTROL ELEVATIONS SHOWN TO THE NEAREST 0.1 METER
OTHER ELEVATIONS SHOWN TO THE NEAREST METER
To convert meters to feet multiply by 3.2808
To convert feet to meters multiply by 0.3048

THIS MAP COMPLIES WITH NATIONAL MAP ACCURACY STANDARDS
FOR SALE BY U S. GEOLOGICAL SURVEY, DENVER, COLORADO 80225, OR RESTON, VIRGINIA 22092

QUADRANGLE LOCATION

1	2	3	1 North Palisade 2 Split Mtn. 3 Fish Springs 4 Marion Peak 5 Aberdeen 6 The Sphinx 7 Mt. Clarence King 8 Kearsarge Peak
4		5	
6	7	8	

ADJOINING 7.5' QUADRANGLE NAMES

CONTOURS AND ELEVATIONS IN METERS

ROAD LEGEND
Improved Road
Unimproved Road
Trail
Interstate Route U.S. Route State Route

MT. PINCHOT, CALIF.
PROVISIONAL EDITION 1985
36118-H4-TM-024

Appendix V

Data for Water Chemistry and Presence/Absence of Amphibians and Fish in the 33 Lakes of the Detailed Survey

Appendix V. Data for water chemistry and presence/absence of amphibians and fish in the 33 lakes of the detailed survey.[1]

LAKE ID	DATE	pH(TJ)	pH(FS)	ANC µeq/l	EC(TJ) µS/cm	EC(FS) µS/cm	R.m. Tad	R.m Ad	O.m.	O.a.	S.t.	S.f.
B-1A	8/15/92	7.54	7.28	108	25.30	26.2	-	+	+	-	-	-
B-1B	8/15/93	7.67	7.43	124	25.10	26.4						
B-5	8/15/93	6.49	6.33	15	4.63	5.3	+	+	-	-	-	-
C-2	8/13/93	8.25	8.23	322	126.10	145.0	+	+	-	-	-	-
C-4	8/13/93	6.91	6.83	122	26.90	31.6	-	-	+	-	-	+
C-24	8/13/93	5.09	4.73	-14	49.50	57.6	-	-	-	-	-	-
C-22	8/13/93	5.60	5.27	-0.4	40.70	47.5	-[2]	+	-	-	-	-
C-21	8/13/93	6.90	6.90	62	25.30	30.7	-	-	-	-	-	+
C-23	8/13/93	7.34	7.10	215	62.10	74.4	-	-	-	-	-	-
C-10	8/14/93	7.53	7.38	130	24.70	22.7	+	-	-	-	-	-
C-17	8/14/93	7.80	7.20	99	19.99	22.0	+[2]	+	-	-	-	-
C-5	8/14/93	7.26	6.90	56	12.32	10.9	-	+	-	-	-	+
D-5	8/21/93	6.68	6.46	29	21.80	24.0	-	-	-	-	-	-
D-4	8/21/93	7.04	6.72	43	34.10	37.0	-	-	+	-	-	-
E-1	8/22/93	7.02	6.91	94	16.62	16.6	-	-	+	-	+	-
E-4	8/22/93	6.85	6.53	44	8.77	9.0	+	+	-	-	-	-
F-2	8/22/93	5.05	4.86	0.5	65.40	75.8	-	+	-	-	-	-
F-1	8/22/93	5.29	5.00	-3	57.90	68.4	-	+	-	-	-	-
F-4	8/23/93	7.03	6.57	73	17.29	17.5	+	+	-	-	-	-
F-14	8/23/93	5.37	5.30	1	30.10	31.8	-	+	-	-	-	-
F-13N/A	8/23/93	5.91	5.77	5	42.80	44.6	-	+	-	-	-	-
F-13N/B	8/23/93	5.82	5.64	-0.5	41.70	44.5						
F-11	8/23/93	6.64	6.24	15	31.80	33.8	+	+	-	-	-	-
F-13S	8/23/93	6.98	6.62	50	40.30	41.6	+	+	-	-	-	-
F-12	8/23/93	8.61	7.59	276	116.40	120.8	+	+	-	-	-	-
L-11	8/31/93	5.99	5.96	6	38.80	40.4	-	-	-	-	-	-
L-9	8/31/93	6.99	7.02	86	51.70	54.9	-	-	-	-	-	-
L-8	8/31/93	6.72	6.64	49	50.10	52.5	-	-	-	-	-	-
L-7	8/31/93	4.78	4.72	-6	78.40	82.5	-	-	-	-	-	-
L-1A	8/31/93	6.61	6.65	30	12.29	13.0	+	-	-	-	-	-
L-1B	8/31/93	6.87	6.64	26	12.15	13.0						
N-3	8/25/93	7.29	6.93	91	31.20	33.5	+[2]	+	-	+	-	-
O-21	8/25/93	7.15	6.90	77	16.02	15.2	+[2]	+	-	-	-	-
P-3	9/1/93	7.55			22.70		-	-	-	-	-	-
O-8	8/25/93	7.58	7.23	200	27.90	29.8	-[2]	+	-	-	-	-
O-7	9/1/93	8.50			53.10		-	-	-	-	-	-

[1]A and B for lake ID's indicate that replicate samples were taken
Water chemistry data are from Appendix III.
pH and conductivity (EC): pH and EC marked "TJ" were measured in the field; those marked "FS" were measured on duplicate samples at UCSB.
Yellow-legged frogs: R.m. Tad refers to tadpoles. R.m. Ad refers to metamorphosed individuals of any size.
Fish: O.m. = rainbow trout; O.a. = golden trout; S.t. = brown trout; S.f. = brook trout.

[2]Difficult viewing conditions. Presence/ansence of tadpoles was assumed to be same as Synoptic Survey because tadpoles require 2-3 summers to reach metamorphosis at high elevation.

Appendix V (continued). Data for water chemistry and presence/absence of amphibians and fish in the 33 lakes of the detailed survey.[1]

LAKE ID	DATE	Cl^- µeq/l	NO_3^- µeq/l	SO_4^{-2} µeq/l	NH_4^+ µM	R.m Tad	R.m Ad	O.m.	O.a.	S.t.	S.f.
B-1A	8/15/92	6	5.6	98.6	0.6	-	+	+	-	-	-
B-1B	8/15/93	4.4	5.0	97	0.3						
B-5	8/15/93	3.8	1.2	12.7	0.4	+	+	-	-	-	-
C-2	8/13/93	8	0.1	869	0.1	+	+	-	-	-	-
C-4	8/13/93	4.1	2.3	178	0	-	-	+	-	-	+
C-24	8/13/93	4.7	12.4	442	1	-	-	-	-	-	-
C-22	8/13/93	5.2	10.8	406	1	-[2]	+	-	-	-	-
C-21	8/13/93	3.4	2.0	190	0	-	-	-	-	-	+
C-23	8/13/93	23.5	26.0	367	0.8	-	-	-	-	-	-
C-10	8/14/93	3.6	1.4	42.3	1.2	+	-	-	-	-	-
C-17	8/14/93	3.4	1.6	57.2	0.8	+[2]	+	-	-	-	-
C-5	8/14/93	2.7	0.3	22.7	0	-	+	-	-	-	+
D-5	8/21/93	5.5	22.8	119	0.6	-	-	-	-	-	-
D-4	8/21/93	4.2	10.2	232	0	-	-	+	-	-	-
E-1	8/22/93	3.7	2.0	46.6	0.6	-	-	+	-	+	-
E-4	8/22/93	8.8	0.1	17.5	0.4	+	+	-	-	-	-
F-2	8/22/93	4.7	9.7	560	0.3	-	+	-	-	-	-
F-1	8/22/93	4.4	10.3	578	0.3	-	+	-	-	-	-
F-4	8/23/93	5.7	0.2	57.7	0.3	+	+	-	-	-	-
F-14	8/23/93	4.7	25.8	250	0.8	-	+	-	-	-	-
F-13N/A	8/23/93	4.7	15.0	338	0.5	-	+	-	-	-	-
F-13N/B	8/23/93	4.7	15.4	348	0.9						
F-11	8/23/93	6.5	10.0	252		+	+	-	-	-	-
F-13S	8/23/93	3.7	3.8	273	2.8	+	+	-	-	-	-
F-12	8/23/93	7.7	0.2	820	1.2	+	+	-	-	-	-
L-11	8/31/93	7.7	26.2	278	0.6	-	-	-	-	-	-
L-9	8/31/93	4.2	11.6	334	1.1	-	-	-	-	-	-
L-8	8/31/93	5.7	9.9	365	0.1	-	-	-	-	-	-
L-7	8/31/93	11.1	8.3	620	0.6	-	-	-	-	-	-
L-1A	8/31/93	2.6	1.6	69.3	0.2	+	-	-	-	-	-
L-1B	8/31/93	2.6	1.6	67.2	3.2						
N-3	8/25/93	2.6	0.2	175	0.2	+[2]	+	-	+	-	-
O-21	8/25/93	2.2	0.2	38.5	0	+[2]	+	-	-	-	-
P-3	9/1/93	2.9	1.8	37.2	0	-	-	-	-	-	-
O-8	8/25/93	2.3	0.0	48	0	-[2]	+	-	-	-	-
O-7	9/1/93	7.9	0.0	40	0	-	-	-	-	-	-

[1]A and B for lake ID's indicate that replicate samples were taken
Water chemistry data are from Appendix III.
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Fish: O.m. = rainbow trout; O.a. = golden trout; S.t. = brown trout; S.f. = brook trout.

[2]Difficult viewing conditions. Presence/ansence of tadpoles was assumed to be same as Synoptic Survey because tadpoles require 2-3 summers to reach metamorphosis at high elevation.

Appendix V (concluded). Data for water chemistry and presence/absence of amphibians and fish in the 33 lakes of the detailed survey (concluded).

LAKE ID	DATE	Ca µeq/l	Mg µeq/l	Na µeq/l	K µeq/l	Al µeq/l	R.m Tad	R.m. Ad	O.m.	O.a.	S.t.	S.f.
B-1A	8/15/92	195	20.8	22	10.7	1.08	-	+	+	-	-	-
B-1B	8/15/93	196	19.7	22	10.7	0.87						
B-5	8/15/93	14.3	3.3	9.1	4.5	0.95	+	+	-	-	-	-
C-2	8/13/93	972	30	322	10	2.46	+	+	-	-	-	-
C-4	8/13/93	216	35.8	24	7.1	2.38	-	-	+	-	-	+
C-24	8/13/93	185	117	28	9	75.1	-	-	-	-	-	-
C-22	8/13/93	204	104	30	11	21.9	-[2]	+	-	-	-	-
C-21	8/13/93	194	35	22	6.8	1.36	-	-	-	-	-	+
C-23	8/13/93	530	35	21	12.5	1.02	-	-	-	-	-	-
C-10	8/14/93	189	15.3	12	7.9	1.1	+	-	-	-	-	-
C-17	8/14/93	143	16.7	14	8.9	3.16	+[2]	+	-	-	-	-
C-5	8/14/93	59.4	11	16	6.9	0.66	-	+	-	-	-	+
D-5	8/21/93	162	11.4	21	4.9	2.15	-	-	-	-	-	-
D-4	8/21/93	242	15.6	30	4.1	5.28	-	-	+	-	-	-
E-1	8/22/93	115	6.4	25	5.3	1.08	-	-	+	-	+	-
E-4	8/22/93	39.4	7.4	25	6	8.73	+	+	-	-	-	-
F-2	8/22/93	288	162	55	24.5	73.7	-	+	-	-	-	-
F-1	8/22/93	247	146	49	22.5	53.3	-	+	-	-	-	-
F-4	8/23/93	120	9.3	21	5.2	1.28	+	+	-	-	-	-
F-14	8/23/93	142	39.5	29	15.5	8.64	-	+	-	-	-	-
F-13N/A	8/23/93	193	59	52	25	7.57	-	+	-	-	-	-
F-13N/B	8/23/93	193	57	51	25	7.31						
F-11	8/23/93	157	42	39	17	3.11	+	+	-	-	-	-
F-13S	8/23/93	242	41.5	35	17	3.4	+	+	-	-	-	-
F-12	8/23/93	787	104	93	28	5.56	+	+	-	-	-	-
L-11	8/31/93	216	43.5	40	14.8	5.33	-	-	-	-	-	-
L-9	8/31/93	345	54	11	2.4	3.68	-	-	-	-	-	-
L-8	8/31/93	288	55	52	18	8.43	-	-	-	-	-	-
L-7	8/31/93	272	132	63	20	66.6	-	-	-	-	-	-
L-1A	8/31/93	74.5	8.1	17	6.3	3.05	+	-	-	-	-	-
L-1B	8/31/93	71	8	17	6.3	3.47						
N-3	8/25/93	199	27.4	60	7.8	5.08	+[2]	+	-	+	-	-
O-21	8/25/93	88.5	14.7	25	7.4	5.95	+[2]	+	-	-	-	-
P-3	9/1/93	180	10.3	7.2	6.5		-	-	-	-	-	-
O-8	8/25/93	243	21.1	16	8.2	2.72	-[2]	+	-	-	-	-
O-7	9/1/93	438	36.9	31	21.6		-	-	-	-	-	-

[1]A and B for lake ID's indicate that replicate samples were taken
Water chemistry data are from Appendix III.
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Yellow-legged frogs: R.m. Tad refers to tadpoles. R.m. Ad refers to metamorphosed individuals of any size.
Fish: O.m. = rainbow trout; O.a. = golden trout; S.t. = brown trout; S.f. = brook trout.

[2]Difficult viewing conditions. Presence/ansence of tadpoles was assumed to be same as Synoptic Survey because tadpoles require 2-3 summers to reach metamorphosis at high elevation.

Appendix VI

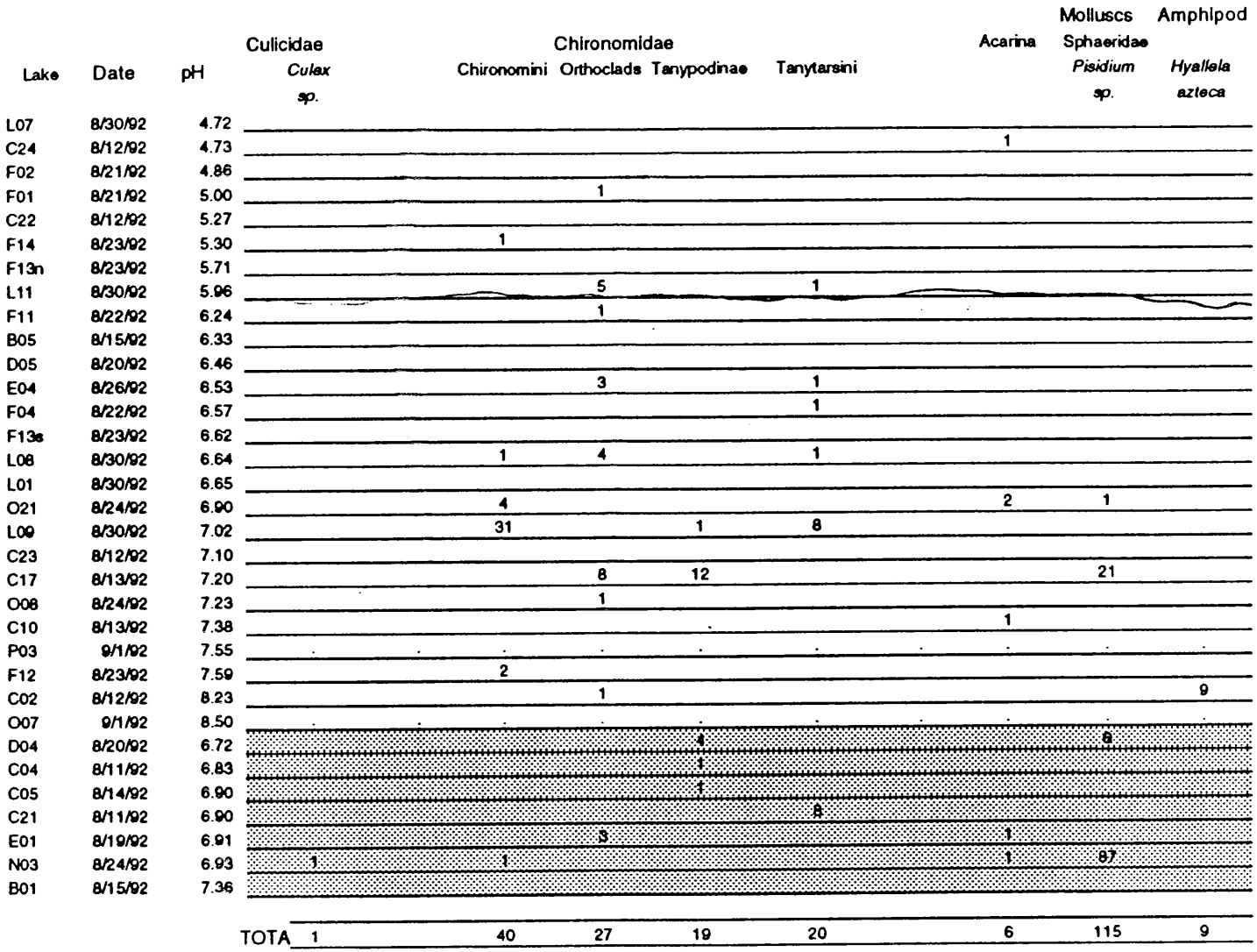
Macroinvertebrates Collected from the Littoral Zone of Lakes in the Detailed Survey

Numbers refer to number of each taxon counted per sample. These data should be interpreted as taxon present (any value given) or taxon absent (blank).

Lake	Date	pH	Fish	Ephemeroptera Baetidae *Baetis sp.*	*Callibaetis sp.*	Siphloneuridae *Ameletus sp.*	Heptageniidae *Cynigmula sp.*	Plecoptera Perlodidae *Isoperla sp.*	Trichoptera Polycentropidae *Polycentropus variegatus*	*Desmona bethula*
L07	8/30/92	4.72	0			24				
C24	8/12/92	4.73	0							
F02	8/21/92	4.86	0							
F01	8/21/92	5.00	0							
C22	8/12/92	5.27	0							
F14	8/23/92	5.30	0							
F13	8/23/92	5.71	0			5				2
L11	8/30/92	5.96	0			4				
F11	8/22/92	6.24	0			2				7
B05	8/15/92	6.33	0							
D05	8/20/92	6.46	0			8				7
E04	8/26/92	6.53	0							
F04	8/22/92	6.57	0			46				
F13	8/23/92	6.62	0							
L08	8/30/92	6.64	0			17				
L01	8/30/92	6.65	0			14				5
O21	8/24/92	6.90	0		5					1
L09	8/30/92	7.02	0	1						2
C23	8/12/92	7.10	0				8			9
C17	8/13/92	7.20	0							11
O08	8/24/92	7.23	0					1		
C10	8/13/92	7.38	0		3	4				
P03	9/1/92	7.55	0							8
F12	8/23/92	7.59	0							
C02	8/12/92	8.23	0		105					
O07	9/1/92	8.50	0							
D04	8/20/92	6.72	1							
C04	8/11/92	6.83	1							
C05	8/14/92	6.90	1							
C21	8/11/92	6.90	1							
E01	8/19/92	6.91	1							
N03	8/24/92	6.93	1						1	
B01	8/15/92	7.36	1						1	
									2	
		TOTA		1	113	124	8	1	4	52

			Coleoptera									
				Limnephilidae		Gyrinidae		Dytiscidae				
Lake	Date	pH	*Ecclisomyia* sp.	*Hesperophylax* sp.	Limnephilid early instar/case	*Gyrinus punctellus*	*Agabus* sp.	*Deronectes* sp.	*Hydaticus modesto*	*Hydroporus* sp.	*Hydrovatus* sp.	*Rhantus* sp.
L07	8/30/92	4.72			1		2	7				
C24	8/12/92	4.73					1	1				
F02	8/21/92	4.86					8	1				
F01	8/21/92	5.00										
C22	8/12/92	5.27					3	4				
F14	8/23/92	5.30										
F13n	8/23/92	5.71					2					
L11	8/30/92	5.96					1					
F11	8/22/92	6.24		4			4	1				
B05	8/15/92	6.33		1			2	12				
D05	8/20/92	6.46		2			1					
E04	8/26/92	6.53				77		1				
F04	8/22/92	6.57		1			7	10				
F13s	8/23/92	6.62										
L08	8/30/92	6.64					1	3				
L01	8/30/92	6.65		5				8				
O21	8/24/92	6.90					4	8		4		
L09	8/30/92	7.02									1	
C23	8/12/92	7.10										
C17	8/13/92	7.20		89			4	7				
O08	8/24/92	7.23		6			2	2				
C10	8/13/92	7.38			2			19				
P03	9/1/92	7.55										
F12	8/23/92	7.59					2	2				
C02	8/12/92	8.23		1			1	16	1			
O07	9/1/92	8.50										
D04	8/20/92	6.72										
C04	8/11/92	6.83										
C05	8/14/92	6.90	1									
C21	8/11/92	6.90										
E01	8/19/92	6.91										
N03	8/24/92	6.93	2	7			1					
B01	8/15/92	7.36						2				1
TOTA			3	116	3	77	46	104	1	4	1	1

Lake	Date	pH	Odonata Coenagrionidae *Enallagma* *sp.*	Megaloptera Sialidae *Sialis* *latreille*	Hemiptera Notonectidae *Notonecta* *spp.*	*Graptocorixa* *spp.*	Corixidae *Hesperocorixa* *spp.*	*Sigara* *salineata/omani/vallis*	Gerridae *Gerris* *spp.*	Dixidae *Dixa* *sp.*
L07	8/30/92	4.72				7			1	
C24	8/12/92	4.73								
F02	8/21/92	4.86					4			2
F01	8/21/92	5.00					1		1	
C22	8/12/92	5.27					3			
F14	8/23/92	5.30					1			
F13n	8/23/92	5.71					1			
L11	8/30/92	5.96								
F11	8/22/92	6.24		1			1			
B05	8/15/92	6.33		1	1		94			
D05	8/20/92	6.46								
E04	8/26/92	6.53	4	1	51		5		1	
F04	8/22/92	6.57				33				
F13s	8/23/92	6.62					28			
L08	8/30/92	6.64					466			
L01	8/30/92	6.65						32		
O21	8/24/92	6.90			1		308			
L09	8/30/92	7.02								
C23	8/12/92	7.10								
C17	8/13/92	7.20				21				
O08	8/24/92	7.23					24			
C10	8/13/92	7.38				7				
P03	9/1/92	7.55								
F12	8/23/92	7.59						55		
C02	8/12/92	8.23		1	1		68			
O07	9/1/92	8.50								
D04	8/20/92	6.72		1						
C04	8/11/92	6.83								
C05	8/14/92	6.90								
C21	8/11/92	6.90								
E01	8/19/92	6.91								
N03	8/24/92	6.93		5						
B01	8/15/92	7.36								
TOTA			4	10	54	68	1004	87	3	2


Lake
Date
pH
Culicidae
Culex sp.
Chironomidae
Chironomini
Orthoclads
Tanypodinae
Tanytarsini
Acarina
Molluscs
Sphaeridae
Pisidium sp.
Amphipod
Hyallela azteca
L07 8/30/92 4.72
C24 8/12/92 4.73
F02 8/21/92 4.86
F01 8/21/92 5.00
C22 8/12/92 5.27
F14 8/23/92 5.30
F13n 8/23/92 5.71
L11 8/30/92 5.96
F11 8/22/92 6.24
B05 8/15/92 6.33
D05 8/20/92 6.46
E04 8/26/92 6.53
F04 8/22/92 6.57
F13s 8/23/92 6.62
L08 8/30/92 6.64
L01 8/30/92 6.65
O21 8/24/92 6.90
L09 8/30/92 7.02
C23 8/12/92 7.10
C17 8/13/92 7.20
O08 8/24/92 7.23
C10 8/13/92 7.38
P03 9/1/92 7.55
F12 8/23/92 7.59
C02 8/12/92 8.23
O07 9/1/92 8.50
D04 8/20/92 6.72
C04 8/11/92 6.83
C05 8/14/92 6.90
C21 8/11/92 6.90
E01 8/19/92 6.91
N03 8/24/92 6.93
B01 8/15/92 7.36
TOTA 1 40 27 19 20 6 115 9

Appendix VII

Zooplankton Densitites (all taxa collected; #/m^3) and Presence/Absence (planktonic species only) in Lakes in the Detailed Survey

Acid Lakes 1992
Zooplankton densities

Lake	Date	pH	Fish	Totcrst	Diapole	Diapshoe	Diaplarg	Diapalg	nauplii	Chyd	Daphm	Daphr	Holop	Boem	Macroth	Polyph	Scapho	Eury	Alona	Totrot
L07	8/30/92	4.72	0	882	0	0	0	0	0	882	0	0	0	0	0	0	0	0	0	7272
C24	8/18/92	4.73	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F02	8/21/92	4.88	0	8	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0	34
F01	8/21/92	5.00	0	8	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0	126
C22	8/12/92	5.27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	65
F14	8/23/92	5.30	0	2472	0	198	198	99	593	1582	0	0	0	0	0	0	0	0	0	325239
F13n	8/23/92	5.71	0	31	0	0	0	23	8	2	0	0	0	0	0	0	0	0	0	35
L11	8/30/92	5.96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	113
F11	8/22/92	6.24	0	54667	0	29	29	42898	11826	118	0	0	0	0	0	0	0	0	0	116
B05	8/15/92	6.33	0	39536	0	0	0	37907	465	233	698	0	0	0	0	0	0	0	233	143721
D05	8/20/92	6.46	0	379	0	152	152	0	8	0	198	0	0	0	23	0	0	0	0	560
E04	8/26/92	6.53	0	83716	0	0	0	69121	3041	0	0	10743	0	0	0	203	0	0	608	191959
F04	8/22/92	6.57	0	80468	0	913	913	68478	10870	65	130	0	0	0	0	0	0	0	0	457
F13e	8/23/92	6.62	0	752	0	106	106	50	57	7	532	0	0	0	0	0	0	0	0	107
L08	8/30/92	6.64	0	57312	0	849	849	38227	20094	0	0	0	0	0	142	0	0	0	0	55613
L01	8/30/92	6.65	0	14117	0	442	442	11484	2014	106	71	0	0	0	0	0	0	0	0	40788
O21	8/24/92	6.90	0	71982	2170	0	2170	60661	6981	0	2170	0	0	0	0	0	0	0	0	47358
L09	8/30/92	7.02	0	27954	0	0	0	341	0	25568	0	0	0	0	0	0	0	0	2045	75882
C23	8/12/92	7.10	0	120	60	0	60	45	0	0	0	15	0	0	0	0	0	0	0	15
C17	8/13/92	7.20	0	6687	0	62	62	3839	2786	0	0	0	0	0	0	0	0	0	0	27988
O08	8/24/92	7.23	0	3362	1648	0	1648	1420	0	0	284	0	0	0	0	0	0	0	0	4205
C10	8/13/92	7.38	0	19197	0	1607	1607	8072	6607	0	4911	0	0	0	0	0	0	0	0	357
P03	9/1/92	7.55	0	112	0	30	30	6	6	0	5	0	0	0	65	0	0	0	0	24
F12	8/23/92	7.59	0	71128	0	0	0	51057	17606	352	0	0	0	0	2113	0	0	0	0	138028
C02	8/12/92	8.23	0	23876	0	0	0	18372	1318	0	0	4186	0	0	0	0	0	0	0	95562
O07	9/1/92	8.60	0	12671	2286	0	2286	571	0	1143	2857	0	0	0	4000	0	0	0	1714	
D04	8/20/92	8.72	1	13019	0	0	0	10189	2830	0	0	0	0	0	0	0	0	0	0	181036
C04	8/11/92	8.83	1	73	0	0	0	0	7	66	0	0	0	0	0	0	0	0	0	2801
C05	8/14/92	8.90	1	11645	0	0	0	6582	506	0	0	380	3291	823	0	0	0	0	63	66012
C21	8/11/92	8.90	1	0			0													0
E01	8/19/92	8.91	1	23330	0	0	0	20960	169	0	0	56	452	584	0	506	621	0	0	184971
N03	8/24/92	8.93	1	58308	0	0	0	51169	484	1452	0	5202	0	0	0	0	0	1	0	23346
B01	8/15/92	7.36	1	17363	0	118	118	7224	9950	47	0	0	0	0	0	0	0	0	24	497

Lake	Date	pH	Lecane	Poly	Hex	Lepad	Trichot	Trichoc	Collo	Cono	Kerco	Kertau	Cephalo	Pomph	Monost	Nothol
L07	8/30/92	4.72	0	7046	0	227	0	0	0	0	0	0	0	0	0	0
C24	8/18/92	4.73	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F02	8/21/92	4.86	0	0	0	30	0	0	0	0	4	0	0	0	0	0
F01	8/21/92	5.00	0	0	0	4	0	0	0	0	0	0	30	91	0	0
C22	8/12/92	5.27	0	0	0	0	4	0	8	0	4	0	8	41	0	0
F14	8/23/92	5.30	0	324843	0	0	99	0	0	0	0	0	0	297	0	0
F13n	8/23/92	5.71	0	0	0	9	15	0	0	0	0	0	0	11	0	0
L11	8/30/92	5.96	0	0	0	113	0	0	0	0	0	0	0	0	0	0
F11	8/22/92	6.24	0	58	0	0	58	0	0	0	0	0	0	0	0	0
B05	8/15/92	6.33	233	137674	0	0	0	0	698	4651	465	0	0	0	0	0
D06	8/20/92	6.46	0	11	0	514	6	23	0	0	6	0	0	0	0	0
E04	8/26/92	6.53	0	19054	0	0	0	83108	0	52297	0	37500	0	0	0	0
F04	8/22/92	6.57	196	261	0	0	0	0	0	0	0	0	0	0	0	0
F13e	8/23/92	6.62	7	60	0	0	43	0	0	0	0	0	0	7	0	0
L08	8/30/92	6.64	0	55613	0	0	0	0	0	0	0	0	0	0	0	0
L01	8/30/92	6.65	0	49682	0	106	0	0	0	0	0	0	0	0	0	0
O21	8/24/92	6.90	0	0	0	0	94	0	0	47264	0	0	0	0	0	0
L09	8/30/92	7.02	1705	341	0	51477	6477	0	0	0	0	0	0	0	15682	0
C23	8/12/92	7.10	0	0	0	0	0	0	0	0	15	0	0	0	0	0
C17	8/13/92	7.20	0	27988	0	0	0	0	0	0	0	0	0	0	0	0
O08	8/24/92	7.23	114	0	0	57	227	0	0	3807	0	0	0	0	0	0
C10	8/13/92	7.38	0	179	0	0	89	0	0	0	0	0	0	0	0	89
P03	9/1/92	7.55	0	0	0	12	0	0	0	0	0	0	0	0	0	12
F12	8/23/92	7.59	0	0	135915	362	1761	0	0	0	0	0	0	0	0	0
C02	8/12/92	8.23	78	388	0	0	0	0	0	0	95116	0	0	0	0	0
O07	9/1/92	8.60														
D04	8/20/92	8.78	0	180766	0	0	94	187	0	0	0	0	0	0	0	0
C04	8/11/92	8.83	180	2447	0	7	7	0	0	0	180	0	0	0	0	0
C05	8/14/92	8.90	83	696	0	0	0	0	949	0	18734	46570	0	0	0	0
C21	8/11/92	8.90														
E01	8/19/92	8.91	0	791	0	0	0	0	11751	153898	13107	6424	0	0	0	0
N03	8/24/92	8.93	484	0	22862	0	0	0	0	0	0	0	0	0	0	0
B01	8/15/92	7.36	142	307	0	24	24	0	0	0	0	0	0	0	0	0

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Acid Lakes 1992
Zooplankton presence/absence

Lake	Date	pH	Fish	Crich	Diapels	Diapsho	Diapsig	Chyd	Daphm	Daphr	Macroth	Alona	Rrich	Lecane	Poly	Lepad	Trichot	Trichoc	Collo	Cono	Kerco	Kertau	Pomph
L07	8/3 /92	4.72	0	1	0	0	0	1	0	0	0	0	2	0	1	1	0	0	0	0	0	0	0
C-24	8/1 /92	4.73	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F02	8/2 /92	4.86	0	1	0	0	0	1	0	0	0	0	3	0	0	1	0	0	0	0	1	0	1
F01	8/2 /92	5.00	0	1	0	0	0	1	0	0	0	0	3	0	0	1	0	0	0	0	1	0	1
C22	8/1 /92	5.27	0	0	0	0	0	0	0	0	0	0	4	0	0	0	1	0	1	0	1	0	1
F14	8/2 /92	5.30	0	3	0	1	1	1	0	0	0	0	3	0	1	0	1	0	0	0	0	0	1
F13n	8/2 /92	5.71	0	2	0	0	1	1	0	0	0	0	3	0	0	1	1	0	0	0	0	0	1
L11	8/3 /92	5.96	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
F11	8/2 /92	6.24	0	3	0	1	1	1	0	0	0	0	2	0	1	0	1	0	0	0	0	0	0
B05	8/1 /92	6.33	0	4	0	0	1	1	1	0	0	1	5	1	1	0	0	0	1	1	1	0	0
D05	8/2 /92	6.46	0	3	0	1	0	0	1	0	1	0	5	0	1	1	1	1	0	0	1	0	0
E04	8/2 /92	6.53	0	3	0	0	1	0	0	1	0	1	4	0	1	0	0	1	0	1	0	1	0
F04	8/2 /92	6.57	0	4	0	1	1	1	1	0	0	0	2	1	1	0	0	0	0	0	0	0	0
F13s	8/2 /92	6.62	0	4	0	1	1	1	1	0	0	0	4	1	1	0	1	0	0	0	0	0	1
L08	8/3 /92	6.64	0	3	0	1	1	0	0	0	1	0	1	0	1	0	0	0	0	0	0	0	0
L01	8/3 /92	6.65	0	4	0	1	1	1	1	0	0	0	2	0	1	1	0	0	0	0	0	0	0
O21	8/2 /92	6.90	0	3	1	0	1	0	1	0	0	0	2	0	0	0	1	0	0	1	0	0	0
L09	8/3 /92	7.02	0	2	0	0	1	1	0	0	0	0	4	1	1	1	1	0	0	0	0	0	0
C23	8/1 /92	7.10	0	3	1	0	1	0	0	1	0	0	1	0	0	0	0	0	0	0	1	0	0
C17	8/1 /92	7.20	0	2	0	1	1	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0
O08	8/2 /92	7.23	0	3	1	0	1	0	1	0	0	0	4	1	0	1	1	0	0	1	0	0	0
C10	8/1 /92	7.38	0	3	0	1	1	0	1	0	0	0	2	0	1	0	1	0	0	0	0	0	0
P03	9/1 /92	7.55	0	4	0	1	1	0	1	0	1	0	1	0	0	1	0	0	0	0	0	0	0
F12	8/2 /92	7.59	0	3	0	0	1	1	0	0	1	0	2	0	0	1	1	0	0	0	0	0	0
C02	8/1 /92	8.23	0	2	0	0	1	0	0	1	0	0	3	1	1	0	0	0	0	0	1	0	0
O07	9/1 /92	8.50	0	6	1	0	1	1	1	0	1	1											
D04	8/2 /92	6.72	1	1	0	0	1	0	0	0	0	0	3	0	1	0	1	1	0	0	0	0	0
C04	8/1 /92	6.83	1	1	0	0	0	1	0	0	0	0	5	1	1	1	1	0	0	0	1	0	0
C05	8/1 /92	6.90	1	3	0	0	1	0	0	1	0	1	5	1	1	0	0	0	1	0	1	1	0
C21	8/1 /92	6.90	1	0	0	0	0	0	0	0	0	0	3	0	1	0	1	0	0	0	1	0	0
E01	8/1 /92	6.91	1	2	0	0	1	0	0	1	0	0	5	0	1	0	0	0	1	1	1	1	0
N03	8/2 /92	6.93	1	4	0	0	1	1	0	1	0	1	1	1	0	0	0	0	0	0	0	0	0
B01	8/1 /92	7.36	1	4	0	1	1	1	0	0	0	1	4	1	1	1	1	0	0	0	0	0	0
				TOTALS	4	11	24	16	10	8	5	6		10	20	13	15	3	4	5	11	3	6
	AVG RICH:			2.5								AVG RI	2.8										

"AVG RICH" represents average species richness for crustaceans ("Crich") and rotifers ("Rrich").