

Snowpack Acidity in the Colorado Rocky Mountains

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ABSTRACT

The present study examines the pH and specific conductivity values of snowpack samples taken from around the state of Colorado. Snowpack sampling is a useful tool for several reasons. 1) The majority of the precipitation at higher elevations in Colorado falls as snow during the winter months, building the winter snowpack, which then remains until the spring thaw. 2) The snowpack has the advantage of being the accumulated total of the winter season's precipitation, which preserves ionic constituents, including acids, until the first runoff takes place. Because of this property, a site can be sampled at a single time and a profile of the entire season's precipitation can be obtained. Sampling sites were chosen throughout the mountain regions of the state such that some would potentially be affected by local sources of acidic pollutants, such as coal-fired power plants or the Front Range Urban Corridor, and others would likely be free from such effects and represent the amount of acid entering the state from the west.

The most significant feature of the study is the baseline of pH and conductivity information established on the wintertime precipitation in the Colorado Rockies. This information has covered a broad area of the state and a variety of conditions. It has shown that none of the pH values were extremely low or extremely high.

Because of the presence of local sources of acidic pollution near some of the sites and the absence of local effects at other sites, the relative importance of local effects versus long range transport to the measured pH values can be inferred. Samples from sites near local sources of acid pollutants that receive a maximum in orographic precipitation enhancement when directly downwind from the source, exhibited the

most consistently low pH values. Samples from sites free from local effects, "clean" sites, showed higher pH values. These "clean" sites on the western edge of the state had a few low pH values, suggesting that sporadic intrusions of acidic contaminants come into the state. "Clean" sites in the central mountains had relatively high pH values overall, indicating that acidic contaminants are washed out by the time the precipitating air mass reaches the site. Therefore, local sources seem to dominate the low pH values at individual sites.

The "clean" sites on the western edge of the state also have more pH values above 5.6, suggesting that alkaline components, potentially from the alkaline soils of the Great Basin, may play a significant role in the total acidity measured. Therefore, acidic contaminants may be transported over long ranges, but not be detected because they are being neutralized by alkaline components. In the absence of the alkaline soils of the Great Basin, the total acidity measured might be much greater in the region.

In addition to these major points, some secondary observations and conclusions were also made. These include ion migration with the initial meltwater within the snowpack, the absence of effect on the pH or conductivity from the ash fallout of the Mt. St. Helens eruption, the lack of correlation between pH and conductivity, the utility of the sampling and analysis technique, the variations of pH with snow type, and comparison with other snow and pH measurements in other parts of the world.

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CHAPTER 1 INTRODUCTION

1.1 Background

Acid precipitation is natural precipitation which has a pH* value less than what one would expect from natural ambient conditions. The pH value expected in natural, unaltered precipitation is not, however, 7.0, the defined value for pure, distilled water. Distilled water is an excellent solvent and consequently is able to dissolve atmospheric carbon dioxide, forming carbonic acid. Under normal atmospheric conditions, the equilibrium amount of CO₂ dissolved in distilled water will form carbonic acid with a pH value of 5.6. Hence, acid precipitation is defined as precipitation whose pH value falls below 5.6.

Acid precipitation has been a recognized phenomenon for many years. It was first identified by an English chemist in 1872. Swedish scientists were the first to conduct systematic investigations on this topic. In July 1953, a network of heated rain-gauges was set up in Sweden to sample for acid precipitation; prior to this time only spot observations had been made (Barrett and Brodin, 1955). The network was expanded in November 1954 to become pan-Scandinavian. The data from this network identified a minimum in the pH of precipitation during February and March. The weighted mean pH during this time was between 4.7 and 4.8. The analysis of this data showed the minimum to coincide well with a prevailing air flow from over the industrialized regions of Europe to the south, in addition to the time of maximum combustion of fossil fuel for heating in the area. Hence, long range transport seemed to be a contributing factor to the acid precipitation phenomenon.

* $\text{pH} = -\log_{10}[\text{H}^+]$, where [] denotes concentration.

During this time period, the chemistry of precipitation was examined in eastern North America (Herman and Gorham, 1957). The average pH value for snow collected in this study was 5.6, the value expected from equilibrium with atmospheric carbon dioxide. Another precipitation sampling network also existed in the eastern U. S. from July 1955 to July 1956, (Likens et al., 1979; Cogbill and Likens, 1974). Data, plotted from this network, demonstrated that most of the precipitation pH values in the northeastern U. S. were below 5.6. Data obtained in 1972 - 1973 (Likens et al., 1979; Cogbill and Likens, 1974) showed that acid precipitation had spread over a much wider area compared with the earlier study, hence, a recent spread of acid precipitation has been accepted. This phenomenon has been linked to long range transport of acidic components from the midwestern United States. It is not entirely clear that the pH drop experienced between 1955 and 1973 is due to increased production of acidic components. Siebel and Semonin (1981) have postulated that the decrease in pH is due to a decrease in alkaline components in the precipitation of the northeast, implying that acid precipitation has been a widespread phenomenon in the eastern United States for a longer period than originally expected.

In spite of the attention that the phenomenon of acid precipitation has been receiving in the past few years, little work has been done in the western United States. In 1964 a complete chemical analysis was undertaken for snow in the Sierra Nevada Mountains and in other regions of the western U. S. (Feth et al., 1964). This analysis showed very few sample values with pH values below 5.0, and most were actually slightly basic. Only quite recently have further investigations indicated the existence of acid precipitation in the western U. S. (Lewis and Grant,

1980). That study indicated some extremely low pH values and indicated a downward trend in pH with time. The investigators suggested that the results of their study indicated widespread acidification of precipitation in the western U. S.

Acid precipitation has gained people's interest because of the potential environmental effects it may pose. This phenomenon has been linked to excessive weathering of stonework and sculpture in Europe; including potential decimation of some ancient ruins. It has also been linked to variations in crop production. These effects are not clear; some crops seem to be hindered by acid precipitation, while others benefit from it. Aquatic ecosystems also tend to be affected by acidic precipitation. In this case the particular precipitation form is snow which results in an acidic snowpack. Areas of Scandinavia and the Adirondack Mountains of New York have experienced fish kills in mountain lakes with a low buffering capacity (Hagen and Langland, 1973; Galvin and Cline, 1978). This has been directly linked to acid precipitation and an acid shock to the aquatic system. The acids within a snowpack tend to stay immobile as long as the snowpack remains cold. When melt occurs, the first meltwater washes the acidic components from the snowpack as it percolates through, becoming enriched with acids (Oden and Bergholm, 1973). The first runoff is more acidic than the average pH of the snowpack and can provide an acidic shock to aquatic ecosystems.

With the postulated hazards associated with acid precipitation and the apparent existence of acid precipitation in Colorado, further study seemed appropriate. The previously mentioned study in Colorado sampled precipitation from only one watershed (Lewis and Grant, 1980). From this, they suggested a widespread acid source from the west. A wider

network certainly seemed desirable to determine the validity of this assumption. They negated, as well, the possibility that the Front Range Urban Corridor to the east could be a likely major source of acidic pollutants to this site, a conclusion which appeared subject to challenge.

To clarify some of these hypotheses and provide a baseline of data, snowpack sampling would be a useful tool for several reasons. 1) The majority of the precipitation at higher elevations in Colorado falls as snow during the winter months, building the winter snowpack, which then remains until the spring thaw. 2) The snowpack has the advantage of being the accumulated total of the winter season's precipitation, which preserves ionic constituents, including acids, until the first runoff takes place. Because of this property, a site can be sampled at a single time and a profile of the entire season's precipitation can be obtained. Experimentally this can be of great advantage in the remote mountain regions of the Rockies.

1.2 Objectives and Approach

The primary objectives of this study were to 1) determine the regional extent of wintertime acid precipitation in the state of Colorado, 2) consider the potential contributing sources of acid, and 3) establish a baseline of data for further studies. Secondary objectives included determining the variations in acidity with elevation, the effect of the spring melt on the acidic content of the snowpack, and the annual variability of acids in the snowpack.

The basic questions in determining the extent of the acid precipitation problem in Colorado were: Is the problem widespread and where does a problem specifically exist? To facilitate answering these questions a wide network of sampling sites is needed. Hence, sites were

chosen throughout the mountain regions of the state (Figure 1.1). At each site snowpits were dug and after the wall of the pit was scraped clean, samples were taken. These samples were then transported back to the laboratory in a frozen state for analysis of pH and conductivity.

If acids were found, then sources become the next question. The sources of acids to a site would be from either long range transport, such as that experienced in Scandinavia or the northeastern U. S., or from acid emitters within close proximity to the site. In order to distinguish between these two possibilities, some sites were chosen downwind of potential areas of localized acidic emissions such as power plants or heavily urbanized areas, while others were chosen such that they would be free from localized effects and represent only the flux of acidic components into the state.

The secondary objectives of this study were addressed by consideration of spacial or temporal variations of pH in the snowpack at the sites. To deal with possible effects from elevation differences of the sites some samples were taken in valleys rather than on ridges, where most sites were located. In other parts of the world there was a pronounced reduction in the hydrogen ion content of the snowpack after runoff initiated. To investigate whether a similar situation occurs in Colorado and to what extent it occurs, samples were collected at two of the original sites later in the spring, after the first sampling period. Annual variability is, of course, a question raised from any data set taken in only one season. To deal with this, samples were taken at most of the sites the following year in the same manner.

Possibly the most useful information provided by the study at hand is a baseline of data for comparison with future studies. The present

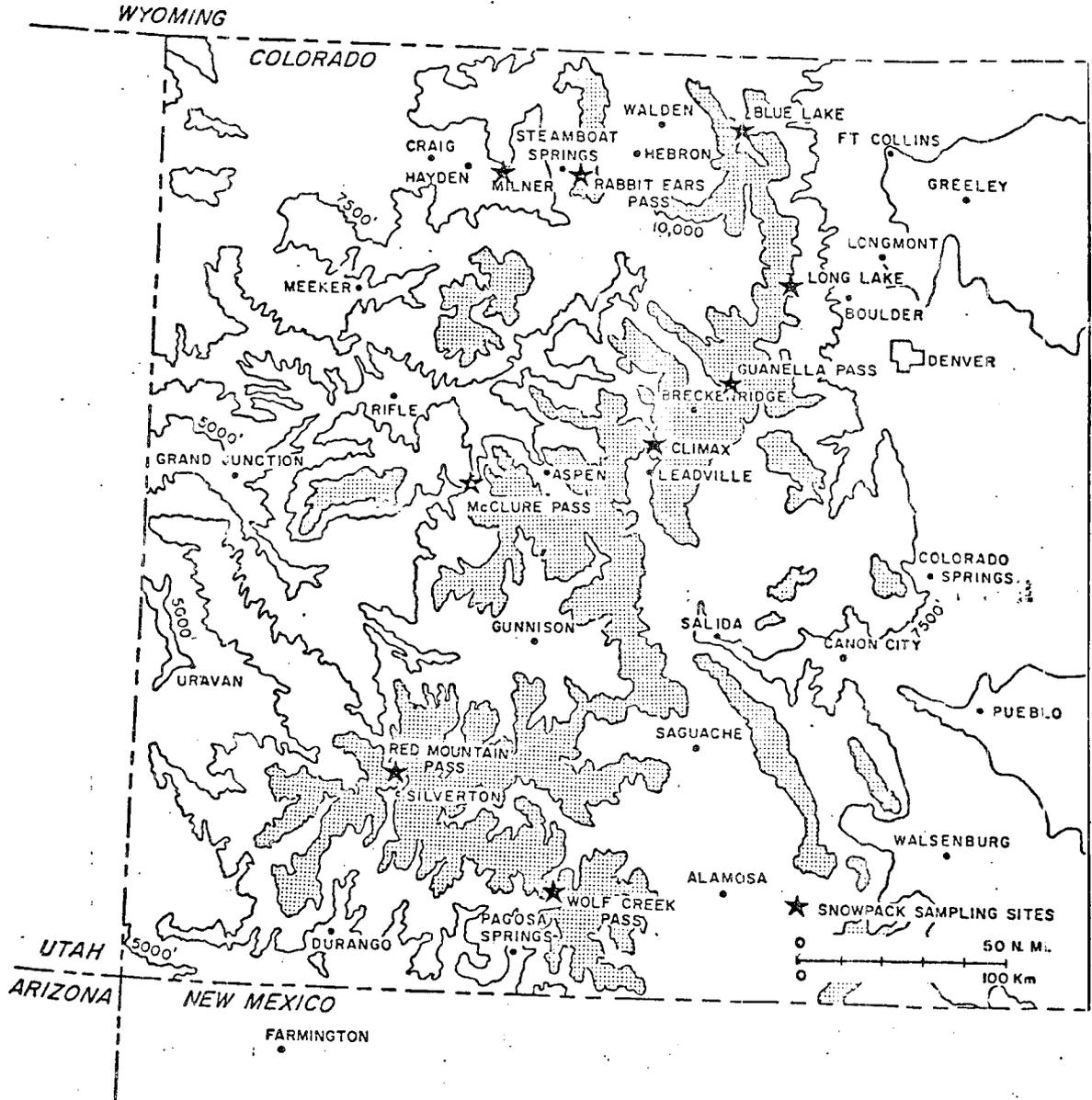


Figure 1.1. Map of the mountain regions of Colorado. The stars indicate the primary snowpack sampling sites.

study contains data which provide variations of acidity at each site and between sites. The scope of the site network is large enough and varied enough to give a general overview of the acid precipitation phenomenon in the mountain regions of Colorado.

1.3 Literature Review

The literature on the general phenomenon of acid precipitation is quite varied and extensive. Most of this literature does not relate directly to the study at hand, hence it will be omitted from this discussion. The material which will be discussed either pertains to acids and other ions found in snow, mechanisms by which ions can become incorporated with snow, environmental effects resulting from acidic snow, or acid precipitation observations found in the area of study. The ultimate goal of the studies mentioned was not always a study of acid precipitation itself. Often, pH observations were incidental to other studies. These studies varied from nivation (rock weathering) studies and the effects of chemical weathering, to ice cores taken in general precipitation chemistry studies. The subject of acid precipitation bridges a variety of fields, hence, the literature cited comes from a variety of sources.

The discussion that follows will be a summary of the individual articles in terms of what is significant to the present study. This will include, when appropriate; sampling technique, analysis technique, geographic area of study, purpose of the study and results. With the general background of each study, a comparison with the present study will be made noting similarities and differences.

Early Studies: The early studies in Scandinavia and northeastern Canada (Barrett and Brodin, 1955; Herman and Gorham, 1957), were discussed pre-

viously. At that time period, the Scandinavians were finding low weighted mean pH values of 4.7 to 4.8 in the winter months when precipitation would be primarily snow. A Canadian study, on the other hand, found snow pH values to be around 5.6.

The precipitation chemistry networks in the northeastern United States will be discussed in more detail since they have been responsible for much of the interest in acid precipitation in this country. In the 1950's there were no precipitation chemistry sampling networks in the northeastern United States which specifically measured pH. However, stoichiometric relationships have been established to determine precipitation acidity (Cogbill and Likens, 1974). If one assumes 65% of the acid is due to H_2SO_4 , 30% due to HNO_3 , and less than 5% due to HCl, based on recent observations of these compounds, pH values can be predicted from chemical content and will generally agree to within 0.1 pH unit with the observed pH. Using these aforementioned relationships, contour maps of precipitation pH were drawn for the northeastern U. S. for 1955 - 56. These maps show a minimum in pH over the Pennsylvania - New York region. A similar analysis was undertaken for the time period 1965 - 66. During this time period, a south and westward extension of the 5.6 pH contour, the line marking the boundary of acid precipitation, was noted. New England showed a marked drop in pH as compared with the earlier data from 1955 - 56. This study indicates that the northeastern United States has had an acid precipitation problem since the mid-1950's and that the problem is spreading.

These studies have been instrumental in alerting environmentalists to the potential problem of acid precipitation. The implied spread of precipitation acidity has generated much interest in the field

throughout the United States. The exact cause of the problem is not clear. The original hypothesis is that acidic contaminants have been increasing with time and that the source region for the spread of acid precipitation in the New England area is the industrialized regions of the Midwest. Additionally, the relative importance of the principal acids, H_2SO_4 and HNO_3 , has changed (Galloway and Likens, 1981). H_2SO_4 has decreased in precipitation by about 30% with respect to HNO_3 and HNO_3 has increased by about 50% relative to H_2SO_4 . This is attributed to a change in the amount of coal burned versus natural gas. These are all valid measurements and hypotheses. Another possibility has also been raised. This is that the apparent spread in acidity in the eastern United States is not due to an increase in acidic components, but a decrease in alkaline components (measured acidity is a balance between the acidic and the alkaline components)(Siebel and Semonin, 1981). During the time of the precipitation chemistry network used to construct the 1955 - 56 map of precipitation acidity, drought was occurring in the midwestern and northeastern states. Dust storms were a common hazard that year. Dust, being rich in calcium and magnesium, tends to increase the pH value of bulk precipitation. Going back to the data, it was found that the sulfate content of the precipitation remained essentially the same over the years and although nitrate increased it could not account for the marked decrease in pH. What was found was a substantial drop in the alkaline constituents. Using this fact, the predicted pH values were recalculated using more typical values of calcium and magnesium than existed during the time around the 1954 drought. A corresponding map was constructed for the pH distribution at this time. The average pH values all across the country range from less than 4.4 to

5.6, there only being a limited area at the upper end of this spectrum. Because of this, the proposed spread of acid precipitation is not necessarily as great as it might seem. It must be remembered, however, that reconstructed data of this kind is very useful in focusing on a problem and its solution and indicating potential trends, but should not be used to draw solid conclusions.

Until recently it has generally been accepted that the acid precipitation problem has been spreading in the northeastern United States. There was no indication, however, what the situation was in the western U. S., that is: Had acid precipitation spread that far? This question evidently lead to a study in the Como Creek watershed on the eastern slope of the Colorado Rocky Mountains, west of Boulder, Colorado (Lewis and Grant, 1980). Two bulk precipitation collectors, one kilometer apart, located at an elevation of 2900 meters, six kilometers east of the continental divide, were used. From a three year data set of bulk precipitation, collected at weekly intervals, the authors found a downward trend in pH and an increase in nitrogen compounds. Linear regression performed on the data, using pH as the dependent variable and the week number of the study as the independent variable, indicates that the average pH at the beginning of the study was 5.43 with a standard error of 0.11, which declined at an average rate of 0.0053 pH units per week with a standard error of 0.0013 over the succeeding three year period; or by the end of the three year period the average pH had declined by 0.80 pH units from 5.43 to 4.63. Similar results were found for the nitrogen compound increase, while sulfate showed no significant trend. This suggested that sulfuric acid may be a major contributor to the total acidity, but nitric acid was responsible for the trend.

From their analysis, Lewis and Grant (1980) concluded that their results indicated wide spread acidification of precipitation in the western United States. This conclusion was based on the following:

- 1) The climatology of Niwot Ridge shows air movement to be predominantly from the northwest (Barry, 1972), a region of low population density.
- 2) Upslope events are sporadic, common only to the spring and summer, and are then interrupted by long periods of southeasterly (sic) [northwesterly] flow over the divide. Therefore, they expected the air in this area to receive only sporadic and limited contamination from nearby urban sources of pollution, i. e. the Front Range Urban Corridor.
- 3) Because of the sporadic nature of this source, a downward trend across various times and seasons in the pH could not occur from this source. This reasoning contains some flaws. Climatological data should not be used to determine what happens during a given event or a given year. Secondly, only one small sampling area was used, leaving much room to question the representativeness of this site for the western United States as a whole. Finally and most significantly, a study of NO_x compounds carried out in the same watershed revealed that their concentration increased by a factor of 100 when there was weak upslope flow from the east to this site (Kelly and Stedman, 1980).

These results indicated that there was acid precipitation in Colorado. The extent of the problem was unclear. Because of the lack of clarity, further study seemed warranted. Accordingly, the present study was undertaken. The advantages of the snowpack in Colorado for precipitation acidity sampling were mentioned earlier. The following review is primarily of acids found in snow, the snowpack and the effects unique to this medium.

Acidity in Snow: The oldest records of snow acidity are obtained from ice cores from polar ice sheets, which date back to before the industrial revolution and its effluents. These have yielded varying results. Most studies indicate that the pH values of snow from past times are greater than 5.0 with some between 6.0 and 7.6 (Mellor, 1964; Likens et al. 1979). One study, in particular, examined the acidity of polar ice to determine the effect of volcanic eruptions on the acidity of the cores (Hammer, 1980). The background values of acidity from volcanically inactive periods were found to be pH values of 5.52 to 5.70. Of greater interest, however, was that snowfalls after volcanic eruptions, which in this study dated back to 1380 B. C., varied from 4.64 to 5.30, natural sources which had higher pH values than many values found from more recent polluted sources.

Aside from the historical pH record found in ice cores, the next record of acids in snow is the 1950's, which was mentioned earlier. In the 1960's, there were two studies dealing with snow acidity. One was carried out in the western United States (Feth et al., 1964), the other in the French Alps (Clement and Vaudour, 1967). The former dealt with general chemical constituents of the snowpack, while the latter dealt specifically with acidity.

The western U. S. study took place primarily in the northern Sierra Nevada Mountains of California, with some samples collected from Utah, Denver, Colorado, and other scattered sites (Feth et al., 1964). A fairly complete chemical spectrum was performed on each sample, including pH and conductivity. The samples were obtained by collecting random snow samples with a plastic scoop. These were placed either directly into glass jars or into polyethelene buckets and then stored in glass

jars. These samples were taken from a broad spectrum of sites and snow conditions. In these samples the lowest pH value obtained was 4.2 ranging to some values greater than 8.0. The samples which were obtained from Denver, Colorado, however were all fairly alkaline with respect to equilibrium with atmospheric CO_2 . The pH values were between 6.0 and 7.1. The conductivities of many of the snow samples from the Sierras were between three and eight micromhos, while most of the conductivities of the samples from Denver ranged between 16 and 90, with only one sample as low as 8 micromhos. The conductivity of the Denver samples is typical of what one would expect to find in the precipitation near a polluted urban area while the conductivity of the Sierra samples is typical of clean mountain snows.

A study of very similar nature to the present study was carried out in the southern French Alps during the winter and spring of 1964 - 65 (Clement and Vaudour, 1967). The sampling took place at elevations between 1100 and 2200 meters, slightly lower than the present study. Samples were taken in Pyrex beakers, melted, and measured at the site. Readings were taken as soon as there was sufficient liquid to immerse the electrode. Several interesting things are found in this study. The most frequent pH reading was around 5.4, while the total range in pH values was from 4.4 to 7.0. They found most acidic snows occur during the winter, as opposed to spring. Spring snow pH values had a median value of around 6.0; the widest variation in values occurred at this time. It was found that less dense, powdery snows tended to have lower pH values than denser, wetter, more granular snows, although there is wide variation in the values obtained.

Recently, in connection with a nivation study, snow samples from Niwot Ridge in Colorado were analyzed for pH (Thorn and Hall, 1980). The samples analyzed from this study had pH values ranging between 4.5 and 5.5.

A need for acidity data from an area fairly free from any anthropogenic effects was the motivation for obtaining samples from northern Africa (Brimblecombe, 1980). The mountains of northern Africa receive snowfall from wind directions which do not cross large industrialized regions, hence, should be relatively free from the effects of anthropogenic effluents. The pH values found in this region fell between 5.2 and 6.7. The unpolluted snow in this area showed little effect of acidification.

Effects of Melt: In the late 1960's, some snowfalls in southern Norway were so polluted that they were actually a dark grey color when they fell (Elgmork et al., 1973). Consequently, there were grey bands of snow in the snowpack when snowpits were dug for snowpack sampling. The grey bands allowed one to identify a specific snowfall event over a wide area. It was found that these grey layers had lower pH values and higher conductivities than did the white bands. The pH values from a grey snowfall, which occurred on 5 January 1969, varied over a large area from pH values of 3.8 to 4.8. To determine the extent of ion mobility in the snowpack, small samples were collected as well as bulk samples. The small samples revealed that the snowpack showed discrete peaks in pH and conductivity, that is a layer directly adjacent to a layer with low pH, i. e. a grey layer, could have a much different pH, unless melt occurred. Reliability checks were run throughout their experiment. At one sampling station, near a city, fresh snowfall was

analyzed and compared with results taken later in the winter. The indications from this comparison were that the peak values in the freshly fallen snow were the same as those taken later in the winter and from this, that there was little influence from dry fallout, even near the city where the samples were taken. After the first rain occurred in the spring, the chemical differentiation in the snowpack was broken down.

Environmental Effects: A follow up study of Elgmork et al. (1973) was carried out to determine the effects of acidic snowpacks on aquatic ecosystems (Hagen and Langland, 1973). Many Scandinavian lakes are located in pre-Cambrian bed-rock with acid gneisses and granites. The lake waters are poor in lime and have low pH and buffering capacities, which makes the water systems especially susceptible to acid precipitation.

Snowpack sampling was carried out according to the methods outlined by Elgmork et al. (1973). The snowpack in this study showed pH values ranging from 3.7 to 4.8. After snowmelt initiated, it was found that the pH in the upper layers of a study lake dropped from 5.4 to 4.2 and the conductivity increased from 15 micromhos to 42 micromhos. When pH shocks of this kind occur, they influence the micro-organisms in the lake system as well as fish reproduction.

Another study of snowmelt pH shocks was carried out in Scandinavia in 1969-70, about the same time as the previously mentioned study (Hultburg, 1977). The results of this study showed the pH of the snowpack throughout the area of study to be between 4.4 and 4.5. The snow and ice cover on the lakes studied had pH values as low as 3.7 to 4.0, indicating an acid concentration from the snow via ion concentration at the beginning of snow melt. In 1974, a sharp pH drop occurred in three

lakes from a pH of 5.0 to between 3.8 and 3.4 from a melt period in February.

The acid concentration in the first melt water noted by Oden and Bergholm, (1973) has been studied through further laboratory testing and field experiments in Scandinavia (Johanessen and Henriksen, 1978). Under controlled melting conditions in the laboratory it was found that concentrations of all chemical components were three to five times higher in the first fractions of the meltwater than in the bulk snow, and much lower in the last meltwater fractions than in the bulk snow. This followed for all laboratory samples, despite tenfold differences in the chemical concentrations in the snow samples. The first 30% of the meltwater contained 41 to 80% of the total amounts of all 16 components examined; 61 to 70% of the hydrogen ions were washed out in the first 30% of the meltwater. Using a lysimeter to catch natural snowmelt in the field yielded similar results. During a short warm spell in midwinter, about 15% of the water equivalent of the snowpack was released. In this meltwater about 40% of the total hydrogen ion content was found. After the spring melt started, it was found that the first 30% of the meltwater contained 44 to 76% of the total amount of the 14 chemical components examined. Weekly sampling of the snowpack showed no loss of water or pollutants during the winter before the first melt.

The mechanisms behind this pollutant washout in the first meltwater are also discussed. The main hypothesis put forward is that most pollutants are found on the surface of snow crystals (Johanessen and Henriksen, 1978). The ice crystals are postulated to form in clean air and then adsorb pollutants on their surfaces as the crystals pass through polluted air. This hypothesis does not take into account snowpack

metamorphism and the recrystallization which goes on throughout the life of a snowpack. If indeed the enriched ionic content of the meltwater is due to pollutants being on the surface of the crystals, then the metamorphism process is the most likely mechanism.

Regional studies of the chemical composition of the snowpack have been carried out in Scandinavia as well as the more localized studies just mentioned (Wright and Dovland, 1978). Snowpack samples from this study were taken by digging a snowpit and sampling from the pit wall, as in the study at hand. The amount of acid in the snowpack depended directly upon whether the trajectory of the snowing airmass passed over the major European sulfur emission areas. The snowpack mean pH in southern Scandinavia was less than 4.7, the critical level for fish kills. The results of the study indicated that orographic enhancement of precipitation appeared to diminish acidic components, so that there is less acid precipitation to the lee of a mountain barrier. Comparison was made of snowpack sampling versus chemical precipitation gauges. It was found that chemical concentrations in the snowpack were often much less than concentrations from gauges. Wright and Dovland (1978) concluded from this study that snowpack sampling is a useful tool in providing relative concentration information on a regional basis, but is not a replacement for a precipitation chemistry network. The point should be made, however, that the snowpack is the natural collector of winter precipitation in cold regions, and even though it may differ from the amounts collected in gauges, it is the medium which will affect the individual ecosystems.

Studies similar to the Scandinavian snowpack studies have been carried out in the Adirondack Mountains of upstate New York, where fish

kills have been tied to acid precipitation (Galvin and Cline, 1978; Schofield, 1977). Using snow core samples, kept frozen until analysis could be performed, it was found that nitrate and sulfate were the most dominant anions in the snow, with nitrate being the most abundant, in contrast with Scandinavian snows. The pH values in their samples were all around a pH of 4.2.

Mechanisms for Incorporation of Acids in Snow: The processes by which acidic materials become incorporated in precipitation are not well understood. Most studies have focused on the processes involving liquid water at warm temperatures. These studies have concentrated on chemical reactions involving SO_2 or NO_x since these are the primary acidic components found in acid precipitation (Likens et al., 1979). There is a large gap in the literature of the processes by which acids may become incorporated in snow during formation and fallout. The discussion which follows will briefly address what is published on these processes and how this may affect Colorado winter cloud systems. Some of the processes by which acids may potentially become incorporated in snow are as follows: 1) Diffusion to and adsorption by a growing snow crystal's surface of SO_2 or NO_x gas molecules. 2) Scavenging of H_2SO_4 aerosols during the fall of the snow crystals. 3) Incorporation of acidic cloud droplets to the snow crystal through riming. 4) Or when dealing with snowpack samples, dry deposition on the snowpack surface.

A laboratory study of the scavenging efficiencies of SO_2 gas by snow and ice crystals indicated that the scavenging efficiency of SO_2 is of the order of 4%, which is small as compared with raindrops, which have a scavenging efficiency on the order of 20% (Sood, 1971). This suggests that gas scavenging by snow crystals is fairly inefficient.

Scavenging of H_2SO_4 aerosols by falling will also be inefficient since these will be submicron aerosols which have low collection efficiencies. Submicron particles may, however, be collected by cloud particles through either brownian and eddy diffusion or through diffusiophoresis. Growing ice embryos, with very slow fall velocities, can come into contact with submicron particles through random brownian motions or through the flux of water vapor toward the growing particle, thereby incorporating acidic components in the snow. These effects will be small (Sood, 1971).

The collection of acidic droplets through riming is another possibility for the presence of acids found in snow. The chemical reactions forming both sulfuric and nitric acid are accelerated under conditions of high relative humidity (Cox, 1974). So it would be expected that the formation of these components may be accelerated in clouds. H_2SO_4 also acts as an efficient cloud condensation nucleus (Hegg and Hobbs, 1980). The diffusion of SO_2 gas into liquid water drops is also more efficient, as noted above. The combination of these effects involving liquid water may well make the presence of liquid water during the snow formation process a dominant contributor to finding acids in the snow. In the Colorado Rockies, these mechanisms may be hindered during the winter due to the cold temperatures found in the clouds, which will diminish the rates of reaction of the acid forming processes, and the low liquid water contents found in many of the Colorado mountain clouds. Under stably stratified storm conditions, measured liquid water content values in Colorado wintertime clouds are typically less than 0.1 gm m^{-3} with maximum values reaching up to only 0.5 gm m^{-3} (Rauber, 1981; Cooper and Saunders, 1980). Under neutrally stratified conditions these liquid

water contents typically are about 0.2 to 0.5 gm m⁻³ and under unstable atmospheric conditions, when convection can occur, liquid water content values may approach around 1.0 gm m⁻³ (Cooper and Saunders, 1980). What this implies is that unstable atmospheric conditions are the situations which would be most likely to contribute to acid precipitation through the riming process. A combination of all of the above mentioned mechanisms probably takes part in acid snow formation. Further study is necessary to determine the role of each mechanism individually.

When dealing with snowpack samples, dry deposition may also affect the acidity measured. This mechanism has been studied fairly well. Basically, to obtain an estimate of dry deposition on the snowpack all one has to do is sample new snow right after a snowfall, wait several days during nonprecipitating weather, and sample again. Analysis results are then compared; the difference will be the amount of dry deposition (Forland and Gjessing, 1975; Elgmork et al., 1973). It was found that washout/rainout was generally on the same order as dry deposition near city areas while in the more remote mountain regions the washout was on the order of ten times greater than dry deposition. This seems to be the general trend as brought out through other studies (Likens et al., 1979). Hence, with the exception of areas very near the source of acidic pollutants, wet deposition will dominate the acid precipitation process.

CHAPTER 2 SITE SELECTION, SAMPLING and ANALYSIS

The type and quality of results which are obtained from a snowpack acidity study, such as the one undertaken here, are dependent on the position and type of site selected, the sampling procedure, and analysis techniques used. The first thing to be discussed is the criteria for selecting sites. Following this, the procedure for collecting the data at the various sites is examined. With these procedures in mind, the nature of the individual sites are discussed. Finally, the analysis procedures and techniques are reviewed.

2.1 Site Selection

The main thrust of the present study was to determine whether acid precipitation existed in the Colorado Rockies and to determine whether any acid precipitation found came from a local pollutant source or from long range transport from the west. In order to facilitate the first phase of the study, a wide network of sampling sites was called for. Sites were selected throughout the mountain regions of the state (refer to Figure 1.1). In order to facilitate the second phase of the study, the set of sites was divided into two subsets; those with a known potential local source of acidic pollutants, such as a nearby power plant or the Front Range Urban Corridor, and those with no known localized source of acidic pollution. The sites where local acidic pollutants were expected to dominate were Long Lake, Rabbit Ears Pass, Milner, Wolf Creek Pass and possibly Red Mountain Pass. The sites at McClure Pass and Climax were anticipated to be clean. It was unknown into which category the sites at Guanella Pass and Blue Lake would be likely to fall.

The data quality is highly dependent on the exact location of the sampling site. Acid measurements can be greatly influenced by such things as auto emissions. To avoid this problem, all sites were located well away from roads. The data quality is also dependent on a continually frozen snowpack, therefore, most sites were located at elevations greater than 2750 meters (9000 feet) to ensure a continually frozen snowpack. Some samples were taken at lower elevations from valley sites to determine if any elevation effects did exist.

A problem which is common to the Colorado high country is the relative absence of snow on the ground above timberline, in spite of the fact that the heaviest snowfalls occur at these higher elevations. The snow which falls above timberline is transported away by the wind and is either deposited farther down the slope or more generally is sublimed back into the atmosphere after becoming airborne in high winds (Pope, 1977; Santeford, 1972). Because the wind tends to transport snow away from unprotected areas, the snowpack sampling sites were all selected below timberline in areas sheltered from the wind, but far enough away from vegetation so that it will not affect the samples' chemical composition.

2.2 Sampling Procedure

The sampling containers used were one quart Freezette brand polyethylene freezer boxes with a square cross section of 10.2 X 10.2 cm. Before going into the field, the sampling containers and their lids were washed with distilled, deionized water and numbered.

After the containers had been washed they were taken into the field for sampling. Transportation to the sampling sites from the roadways was accomplished via cross country skis. The sample containers were

carried in a large frame pack. Only 21 sample containers could be carried to a site at one time. Therefore, if the snowpack was too deep to be entirely sampled by 21 containers, part of it remained unsampled.

After skiing in and selecting a site, a snowpit was dug to the ground. The depth of the snowpits varied from 0.91 meters at Milner to greater than 3.5 meters at Wolf Creek Pass, where digging was stopped before the ground was reached, since it became impractical to remove all of the snow from the pit. In digging the pit the snow was all thrown in a direction opposite from the side where samples were to be collected. After the pit was dug, the wall of the pit from which the samples were to be collected was brushed down with a clean polyethylene bag.

At this point sampling was begun by pressing a container into the snowpit wall, removing it with the sample, and sealing the container with its lid. Most containers were then placed into a clean Zip-lock bag. The first samples are taken from the top layers of the snowpack, with the following samples taken contiguously downward. If the snowpack was 1.85 meters deep, or less, the samples were taken contiguously to the bottom of the snowpack. If the snowpack was deeper than this, there was a gap left in the middle, which either remained unsampled or was sampled by scraping one container over the area, with the bottom layers of the snowpack sampled contiguously again. After the sample containers were removed from the pit and placed in Zip-lock bags, they were transported back to the laboratory in a frozen state until analysis could be performed.

2.3 Site Descriptions

When snow samples were collected from each site field notes were taken as to the nature of the snow in the pit, where it lay within the

pit and which sample containers were used to sample the various snow types. Such things as grain type, qualitative description of the density, temperature within the snowpack, the presence of depth hoar, the presence of ice lenses and sun crusts, the crystal habit of newly fallen snow, and the presence of organic matter were noted. In describing the individual sites and the samples from them these things will be included, where applicable, as well as the pertinent geographic characteristics of the site.

February - March Sampling Period

The first set of samples were collected during February and March of 1980. The following is a description of the snowpack characteristics of the sites at that time period.

Long Lake: The Long Lake site is located at an elevation of 3200 meters, 30 kilometers west of Boulder, Colorado. The site is in a clearing along the northwest shore of Long Lake, which is at the base of the north slope of Niwot Ridge. (The sampling site used by Lewis and Grant (1980) was along the south slope of Niwot Ridge.) To the west of the site lies the continental divide. To the east lies the Front Range Urban Corridor, which is a possible contributor of acidic components which may be found at this site. There are certain drawbacks to this site. The structure of the snowpack was dense and fine grained, indicating that the snow had been modified by the wind. This does not allow one to assume that the snow sampled is a continuous sample with respect to time.

The snowpit was dug down to the snow-ground interface on 28 February 1980. The total pit depth was 2.56 meters. The topmost 1.14 meters were sampled, starting at the top, by sample containers 1-13. Then

starting at the bottom and working up contiguously, samples were taken in containers 14-20. Finally a sample was taken in container 21 at the ground-snow interface. The snowpack temperature at 15 cm. depth was -5°C .

Blue Lake: This site is located north of Colorado Highway 14, slightly to the east of Cameron Pass, along the Blue Lake Trail. The elevation of this site is 3000 meters. The pit was dug in a clearing which appeared to have a minimum of alterations in the snowpack due to wind.

The samples were collected on 8 March 1980. The snowpack depth was only 1.55 meters. The sampling containers used were numbers 22 through 39, where samples were taken contiguously from top to bottom, with 39 being the bottom sample. The snowpack here exhibited various density and structure properties. At 0.38 meters a thin ice lens was evident from a clear period when a slight melt took place at the snow surface. At 1.12 meters an abrupt change in density took place; from this depth to the bottom of the pit, there was much depth hoar, giving the lower layers of the snowpack a porous structure. Containers 34 - 39 sampled this porous layer. The snowpack was still below freezing except for right above the snow-ground interface where the temperature was at freezing.

Rabbit Ears Pass: The site is located south of the west summit of Rabbit Ears Pass, in a small clearing in the trees, on the western edge of the Park Range ridgeline. To the west of this site lies the Yampa River valley. Within this valley much energy development is taking place. Presently, there are coal fired power plants operating in Hayden and Craig. Surface strip mining for coal to supply the plants is located

in the area also. The Hayden and Craig plants are located 46 and 68 kilometers west of the sampling site respectively.

The samples were collected from this site on 25 March 1980. The snow depth here was 2.29 meters. Ice lenses from surface melt were found at 0.05, 0.18, 0.69 and 1.65 meters and were collected respectively in containers 40, 42, 48 and 54. The ice lens at 1.65 meters contained much organic matter. This organic matter existed because a dry December experienced in the area, allowed needles from evergreen trees to blow onto the snow and accumulate in one layer. The samples in containers 40 - 52 were taken contiguously from the top down, the sample taken in number 53 was scraped between 1.14 m. and 1.65 m., then 54 was used to sample the layer with organic matter from the December dry spell, with 55 - 60 sampling contiguously below this to the bottom.

Milner: The Milner site is located in the Yampa River valley 19 kilometers ESE of the Hayden Power Plant and 11 km. south of the town of Milner. The site is about one kilometer from a strip coal mine. The elevation of the site is about 2100 meters. This led to some melt in the lower layers which fell prior to the sampling day. The snow depth at this site was only 0.91 meters. The snowpack was at the pressure melting point throughout. A depth of 0.58 meters marked the top of a layer of depth hoar which extended down to the ground. Sample containers 61 -71 were used. Number 61 sampled only the surface layer which fell the night before, number 69 sampled the top layer of depth hoar and 71 was used to sample the bottom layer.

McClure Pass: McClure Pass lies 108 km. east of Grand Junction at an elevation of 2700 meters. Between McClure Pass and Grand Junction lies the Grand Mesa, a high, undeveloped plateau. There is some coal mining

in the area to the south of the pass. For the most part, however, the area is undeveloped.

The snowpack depth at this site was 1.98 meters on 27 March 1980. The snowpack showed no signs of any significant melt. The surface had a 2 cm. sun crust with 13 cm. of powdery snow beneath it. The layer between 15 and 22 cm. showed a significant sun crust. There were several thin melt layers evident below this. Sample containers 72 - 92 were used. The top layer of sun crust was sampled in container 72, then 73 sampled the 13 cm. powdery layer beneath. Number 74 contained the 15 - 22 cm. sun crust. The snowpack was sampled contiguously, below this, down to 1.47 meters, in containers 75 - 89. Container 90 was then scraped between 1.47 m. and 1.75 m., with 91 and 92 sampling the bottom layers. The temperature of the snow was 0°C. at 0.10 m., -2.2°C. at 0.91 m. and -0.3°C. at 1.85 m.

Red Mountain Pass: There were two pits dug at Red Mountain Pass. The first was dug in a slight depression at 3423 meters elevation to the lee of a small hill. At this first site, water was found at a depth of 0.99 meters. With this, it was decided to abandon this site and select another further up the mountain.

A site was selected 37 meters further up the ridge at an elevation of 3460 meters. The snowpack depth at this site on 28 March 1980 was 2.46 meters. There were ice lenses at depths of 24, 28, 38, 41 and 48 cm. The first two were sampled in container 96 with the rest in containers 97, 98 and 99 respectively, all indicating slight surface melt from the sun. At 79 cm. there was a significant feature in the snowpack structure, a layer of clear blue ice. The cause of this is uncertain. The clear blue ice layer was sampled in container 103. Samples were

taken contiguously down to 1.42 meters in numbers 93 - 110, then 11" was scraped between 1.42 and 2.24 meters. Finally, the bottom 23 cm were sampled in numbers 112 and 113.

Wolf Creek Pass: Wolf Creek Pass is located on the continental divide near the New Mexico border. The divide through here runs in a northwest to southeast direction, such that a southwesterly air flow runs normal to the ridgeline. Therefore, any southwesterly storms have a maximum lifting over this region. Also there are no significant physical obstructions southwest of the ridge. These things, coupled with the usual high moisture content of southwesterly storms, gives Wolf Creek Pass some of the highest snowfall totals in the state. This is evidenced by the fact that the sampling pit, dug there on 29 March 1980, was dug down to 3.5 meters and the ground was not reached. This site is located approximately 150 kilometers northeast of the Four Corners Power Plant in Farmington, New Mexico, such that southwesterly flow will bring its effluent in the direction of Wolf Creek Pass.

Due to the great depth of the snowpack at this site, much of it had to remain unsampled. Contiguous samples were taken down to a depth of 1.24 meters in numbers 132 - 147, then spot samples were taken at 1.45, 1.96, 2.72, 3.00 and 3.12 meters in sample containers 148, 149, 150, 151 and 152, respectively. The snow from the lowest three samplings was extremely hard and compact.

Climax: The Climax site is located near Fremont Pass at an elevation of 3450 meters. The sampling site is in a clearing northwest of Chalk Mountain. At this site there is little chance of any acidic constituents influencing the area, being located in the heart of the Rockies in central Colorado. A molybdenum mine, located several kilometers

away, produces no acidic components, although may produce some alkaline components from the nearby settling ponds.

The snowpack at this site was only 1.85 meters deep. The top 5 cm. was comprised of fresh, powdery snow, still showing its stellar structure. Below this layer was 20 cm. comprised of powdery snow which had undergone some equitemperature metamorphism. The top 5 cm. sampled was contained in sample container 153. The next 20 cm. were sampled by 154 and 155. At 25 cm. depth was the first suncrust ice lens, which was sampled in number 156. Below this, the snowpack was fairly homogeneous with only two suncrust layers at depths of 33 cm. and 50 cm. The bottom of the snowpack had a layer of depth hoar around 5 cm. deep. The snowpack temperature was -3.9°C . at 23 cm., -2.2°C . at 1.24 m. and -0.6°C . at 1.84 meters. Samples were taken contiguously in containers 153 - 173 with 173 sampling the bottom depth hoar layer.

Guanella Pass: Guanella Pass is located about 65 km. west of Denver on the Colorado Front Range. The pass is at an elevation of 3500 meters. The sampling site is very close to timberline. To the east of the pass lies a high ridge, along which lie Mts. Bierstadt and Evans, both having an elevation greater than 4300 meters. This poses a significant barrier between the Guanella Pass site and the Front Range Urban Corridor.

The snowpit at this site was excavated on March 31, 1980. Sample containers 174 - 188 were used to sample the 1.35 meter depth, with 174 being the top sample and 188 being the bottom sample. No significant layers existed in the snowpack at this site, with the exception of a shallow depth hoar layer at the bottom of the snowpack, which was collected in container 188. The reason for the homogeneity of the snow is presumably related to the transport to and mechanical alteration of the

snow at the site by the wind. Because of this, the assumption that the snowpit profile is a representation of the time variation of the acids at the site, valid at the other sites, is invalid here.

Miscellaneous Samples: In addition to the systematic samples taken from the snowpits, several more randomly selected samples were taken. One of these, labeled as number 233, was fresh snow collected on a plastic sheet in downtown Steamboat Springs on the night of March 25 - 26, 1980. Samples were also taken from the town of Silverton, Colorado on March 28, 1980 in sample containers 129, 130 and 131, by scooping snow from the snowpack surface in an open field. There were some samples collected from a 61 cm. deep snowpit in the town of Winter Park, Colorado in sample containers 192 - 199 on April 23, 1980. These samples had all undergone some melt.

May 1980 Sampling Period

In order to determine the effects of the spring melt on the pH of the snowpack, samples were collected at Rabbit Ears Pass and Blue Lake, in May 1980 after some melt had occurred. The basic geographic characteristics of these two sites have already been discussed. Hence, the following will contain only pertinent snowpack features.

Rabbit Ears Pass: The site at Rabbit Ears Pass was visited again on May 20, 1980. The snowpack was only 1.37 meters deep at this time and was sampled by containers 204 - 221. Two days before this, Mt. St. Helens violently erupted and sent an ash cloud over the western U. S., part of which fell on the top layer of snow at this site. Sample 204 contains only snow from the top centimeter of the snowpack to determine any potential effects on the acidity of the snowpack from this eruption.

After this, contiguous samples were taken to the base of the snowpack. The snow at this site in late May was wet and granular.

Blue Lake: The site at Blue Lake was visited again on May 21, 1980. By this time the snowpack had been reduced to 0.66 meters. This allowed the entire depth to be sampled in containers 222 - 231. Additionally, sample 232 was used to sample the top centimeter of the snowpack to determine any possible effects on the snowpack acidity from the recent volcanic eruption.

April 1981 Sampling Period

An attempt was made to return to all of the sites, established the previous winter, during the early spring of 1981 to collect data which could be used to determine any annual variability in the snowpack acidity. All of the previous sites were revisited during April 1981, with the exception of Long Lake, Red Mountain Pass and Guanella Pass.

The snowpack depth at all of the sites was greatly reduced as compared with the previous winter. The reason for this is that the state of Colorado experienced a drought during the 1980 - 81 winter season. At the beginning of March 1981, the statewide snowpack in Colorado was only 40% of normal. This improved to 60% of normal by the end of March (Soil Conservation Service, 1981). This low snowpack also led to melt taking place within the snowpack at sites where there was less snow.

Because of the low snowpack and the melt which occurred at many of the sites, the usefulness of the data at some of the sites is greatly diminished due to the ion washout which occurs in a melting snowpack. Therefore, only the sites at Wolf Creek Pass and Rabbit Ear Pass will provide comparative data with the samples from the previous year.

Wolf Creek Pass: The snowpit dug at Wolf Creek Pass was excavated on April 12, 1981. The snowpack at this time was only 1.91 meters deep as opposed to the previous year when the depth was greater than 3.5 meters. The first 23 cm. of the snowpack was mushy, old snow which had undergone some melt; this snow was sampled in containers 301 and 302. Below this there was a soft ice lens, which was sampled in container 303. The remainder of the snowpack below this exhibited no evidence of any melt; this snow was sampled contiguously in sample containers 304 - 319, then 10 cm. was unsampled and the bottom 20 cm. was sampled in containers 320 and 321, the latter being the bottom sample.

At Rabbit Ears Pass, the 1981 snowpit was dug on April 16; the snowpack was 1.52 meters deep. Sampling containers 328 through 330 sampled the partially melted top layers and 331 sampled the soft ice lens marking the boundary between this and the unmelted snow below, which was sampled contiguously in sample containers 332 - 344. To check the reliability of the measurements, four samples were collected from the opposite wall of the snowpit in container numbers 345 - 348, duplicating samples 328 - 331.

Other Sites: The entire snowpack at the remaining sampling sites had undergone some melt, as evidenced by the grain structure and moisture content of the snow. The Blue Lake snowpack was only 46 cm. deep and was sampled in containers 322 - 327. At McClure Pass, the snowpack was 76 cm. deep and was sampled in numbers 349 - 358, while the Climax site was 53 cm. deep and was sampled in containers 359 - 365.

2.4 Sources of Acidic Pollutants in the Study Region

The primary local pollutant sources within the study area are the Front Range Urban Corridor and coal-fired power plants. The Front Range

Urban Corridor's primary pollution source is automobile exhaust emissions, and the principal acidic component of these emissions are the oxides of nitrogen. The coal-fired power plants affecting the study area are in the Yampa River Valley and in Farmington, New Mexico. The plants in the Yampa River Valley are the Hayden Plants 1 and 2 and the Craig Plants 1 and 2. Hayden Plant 1 has a stack height of 76 meters, a base elevation of 1987 meters, a flue gas rate $342 \text{ m}^3 \text{ sec}^{-1}$ and SO_2 and NO_x emission rates of $108.4 \text{ gm sec}^{-1}$ and $166.7 \text{ gm sec}^{-1}$ respectively. The Hayden 2 plant has a stack height of 120 meters, a base elevation the same as Hayden 1, a flue gas rate of $498 \text{ m}^3 \text{ sec}^{-1}$ and SO_2 and NO_x emission rates of 108.4 and $231.6 \text{ gm sec}^{-1}$. Craig plants 1 and 2 both have the same outputs and physical characteristics. The stacks are 183 meters high, the base elevation is 1932 meters, the flue gas rate is $699 \text{ m}^3 \text{ sec}^{-1}$ and the SO_2 and NO_x emissions are 176.8 and $368.7 \text{ gm sec}^{-1}$. The Four Corners Power Plant in Farmington, New Mexico has flue concentrations of SO_2 and NO_x of about 500 ppm.

2.5 Analysis

The snow sample chemical analyses were carried out in a laboratory at the Atmospheric Science Department of Colorado State University. The procedure used was as follows: 1) Samples were removed from the freezer and allowed to melt in their sampling container. 2) A portion of the melted sample, approximately 25 ml., was removed from the container with a clean syringe and placed in a clean, 30 ml. Pyrex beaker. 3) The sample temperature was then taken to correct for temperature deviations of the specific conductivity and pH. 4) Specific conductivity measurement was then made, using a Beckman Model RC16B2 conductivity bridge, with a YSI 3402 conductivity cell with a cell constant of 0.1, and recorded.

5) Measurement of the sample pH was then made, using an Altex 3500 digital pH meter with an Altex 531013 pH combination electrode and recorded. All containers were thoroughly cleaned with distilled, deionized water having a conductivity less than 1 micromho cm^{-1} before each use. The probes were thoroughly rinsed between each measurement with the same.

The pH measurements were automatically corrected for temperature deviations by the meter. The conductivity measurements were all corrected for temperature to a standard of 25°C. with the formula:

$$C_{25} = C_T / (1.0 + 0.025 T)$$

where $T = T - 25$, T being the sample temperature in °C., C_T is the measured conductivity at temperature, T , in micromhos cm^{-1} , and C_{25} is the specific conductivity in micromhos cm^{-1} corrected to 25°C.

CHAPTER 3 RESULTS

Using the analysis techniques described in Chapter 2, the pH and conductivity values for the snow samples were determined. Since the samples were collected with respect to depth in the snowpit, the most logical method of displaying the data is to show the profile of pH or conductivity versus depth. In the figures in this section, the abscissa is marked in units of either pH or conductivity, while the ordinate is marked according to sample number and depth. In general, the sample taken from the ground-snow interface is disregarded since it usually contained some organic matter and soil from the ground.

The median pH value of the samples from each site was determined and this used to segregate the sites, from the first sampling period, into those categorized as clean and those categorized as contaminated. A sharp break can be seen in the spread of the median values between median values of 5.18 and 5.35. The sites with median values less than 5.2 were Rabbit Ears Pass, Wolf Creek Pass, Blue Lake, Milner and Long Lake.

In this chapter, the highlights of the data will be discussed, these in terms of median values or high and low values, then the physical reasons behind the given values will be considered. The results are presented chronologically with respect to the sampling periods.

Before discussing the values from the individual sites, some general comments about the data seem in order. In this study the acidity of the snowpack is of primary concern; the conductivity values are included for an indication of the total free ion amount available in the snow. In the following discussions the pH values will be emphasized.

Throughout the entire study, the lowest sample pH value was 4.63, obtained at Wolf Creek Pass (Figure 3.1a). Interestingly enough, this site also had the least acidic snow sample collected, its pH value being 6.92 (Figure 3.1a). In general, the site at Rabbit Ears Pass showed the most consistently low pH values, while the Climax sampling site showed the most consistently high values.

Statistical analysis, using the Wilcoxon two sample test, was carried out on the data from the mountain sites, taken during the February-March 1980 sampling period. The test was used to determine which sites were statistically similar or different from others.

Overall, there was no correlation between the pH and the conductivity of the snow. Linear regression of the entire data set yielded a correlation coefficient of only 0.355 for pH as a predictor of conductivity. A similarly low correlation was obtained when the pH values and conductivity values for each site individually were regressed against each other. This indicates that hydrogen ions were not the dominating contributor to the total free ion amount.

It should also be noted that the median value of the snow samples at each site was used for comparison purposes, rather than the mean. This is because in order for the mean to be meaningful, the pH values must be weighted according to the water equivalent of the snow. Since the sampling method did not provide samples of uniform cross section, this was not feasible.

3.1 February - March 1980 Sampling Period

During the sampling period of February and March 1980, 188 snow samples were collected from around the state of Colorado from 11 different sites. Of these 188 samples, approximately 21% of them had pH

values below 5.0, 60% were between 5.0 and 5.6, and 19% exhibited pH values in excess of 5.6. Of the 21% which had pH values less than 5.0, 82.5% were from sites considered "contaminated."

For ease of comparison, the results of the first sampling period will be grouped according to whether they are "contaminated" or "clean" sites. The data from Rabbit Ears Pass, Wolf Creek Pass, Blue Lake, Milner, and Long Lake will be presented, followed by the remaining sites, with the some miscellaneous data values reviewed last.

Five of the sites sampled during this period show median pH values less than 5.2, while the remaining sites all have higher median pH values. The difference in the sites with the lower pH medians versus those with the higher median values, is that the former all have an identifiable source of local acidic pollutant. The sites at Wolf Creek Pass, Rabbit Ears Pass, Milner and Blue Lake all are affected by various coal-fired power plants. The fifth site, Long Lake, is affected by the Front Range Urban Corridor. In discussing the sites from this sampling period, the sites affected by coal-fired power plants or the Front Range Urban Corridor will be discussed first, since they are all similar, then the "clean" sites will be discussed.

Wolf Creek Pass: The snow from the Wolf Creek Pass site had similar characteristics to the snow from the Rabbit Ears site, except individual values showed more variability. Here the median pH value was 5.09, the lowest value was 4.63 and the highest was 6.92. These values represent concentrations of hydrogen ions approximately ten times greater and 25 times less than what one would expect from equilibrium with atmospheric CO₂. Nine of the 21 samples from this site had values below 5.0. As seen in Figure 3.1a, the depth of the snow at this site was greater than

three meters, this meant that much of the snowpack remained unsampled. It is quite possible that values exceeding these extremes might have existed, but deeper samples were not collected.

The conductivity values for the snow samples from the Wolf Creek Pass snowpit are shown in Figure 3.1b. The median conductivity of the samples from this site, $7.32 \text{ micromhos cm}^{-1}$ was highest of any of the sites. Wolf Creek Pass also has the highest individual conductivity values in snow samples containing no foreign matter.

The Four Corners Power Plant is located approximately 150 km. southwest of Wolf Creek Pass. Wolf Creek Pass also has the distinction of being one of the areas of highest snowfall in the state of Colorado. The tie between these two facts in relation to this study is that the heaviest snowfall events at Wolf Creek Pass occur when the 700 mb. air flow is from a southwesterly direction, that is, a direction which would allow pollutants from the Four Corners plant to be directly transported to the Wolf Creek Pass area. This phenomenon can be seen in precipitation patterns from an orographic precipitation model (Rhea, 1978). Figure 3.2 shows the model output for 210 degree flow. A maximum in orographic precipitation enhancement at Wolf Creek pass occurs with a southwesterly flow direction. Since southwesterly flow leads to such high snowfall amounts at this site, and since this is the first major barrier northeast of the Four Corners power plant, the effects of pollutants from the plant may be increased due to the orographic enhancement of precipitation here, as discussed earlier. Southwesterly flow does not provide the only precipitation at this site. Orographic precipitation occurs from most wind directions, but here enhancement is not as great from other directions as with southwesterly flow. As was noted in

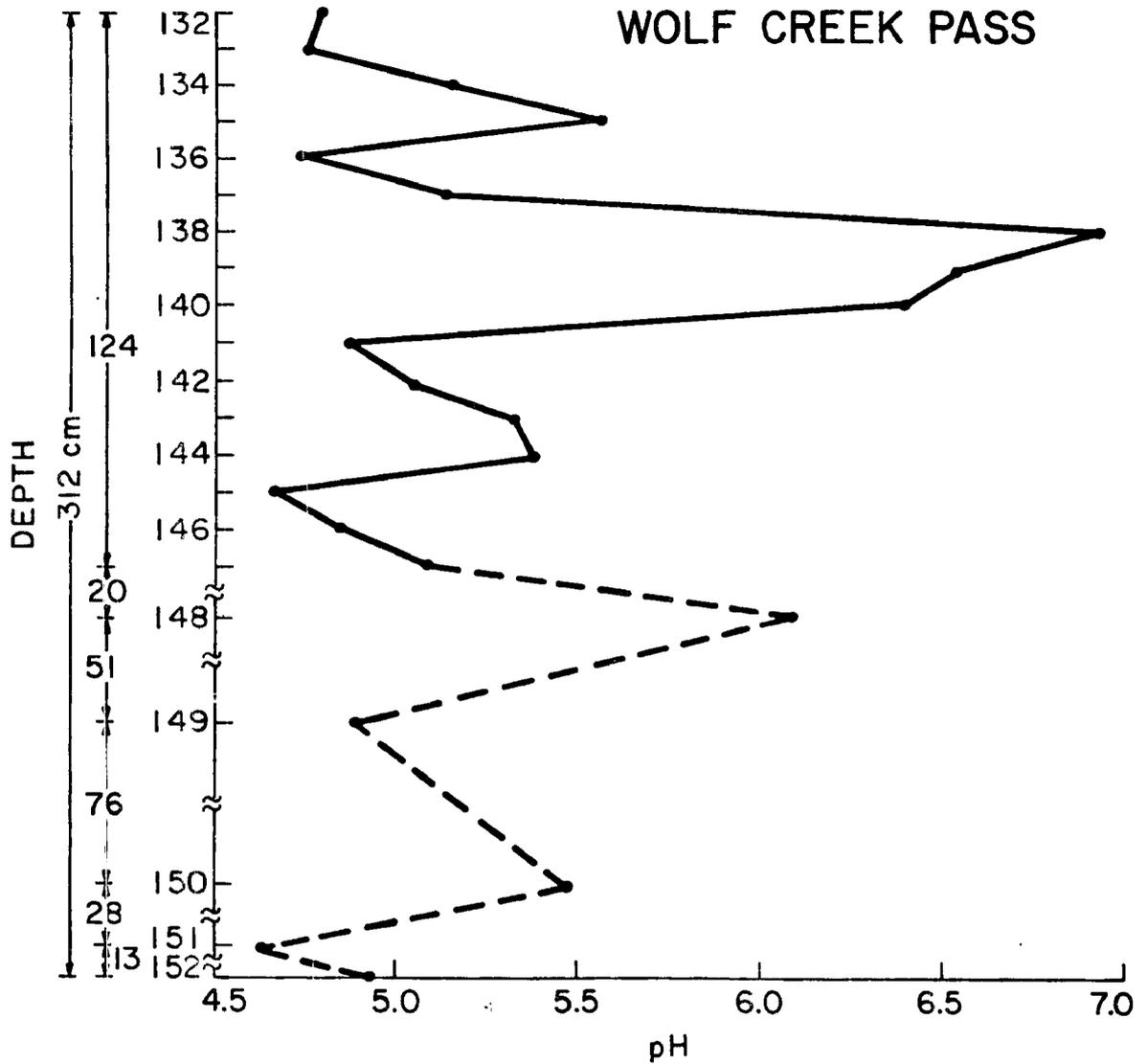


Figure 3.1a. Profile of pH within the snowpack for Wolf Creek Pass. The abscissa is marked in units of pH and the ordinate is marked according to sample number and depth, measured in centimeters. Dashed segments of the profile indicate that the sample at the midpoint of that segment was taken over the distance of that segment and represents the bulk pH value for the depth of the dashed segment.

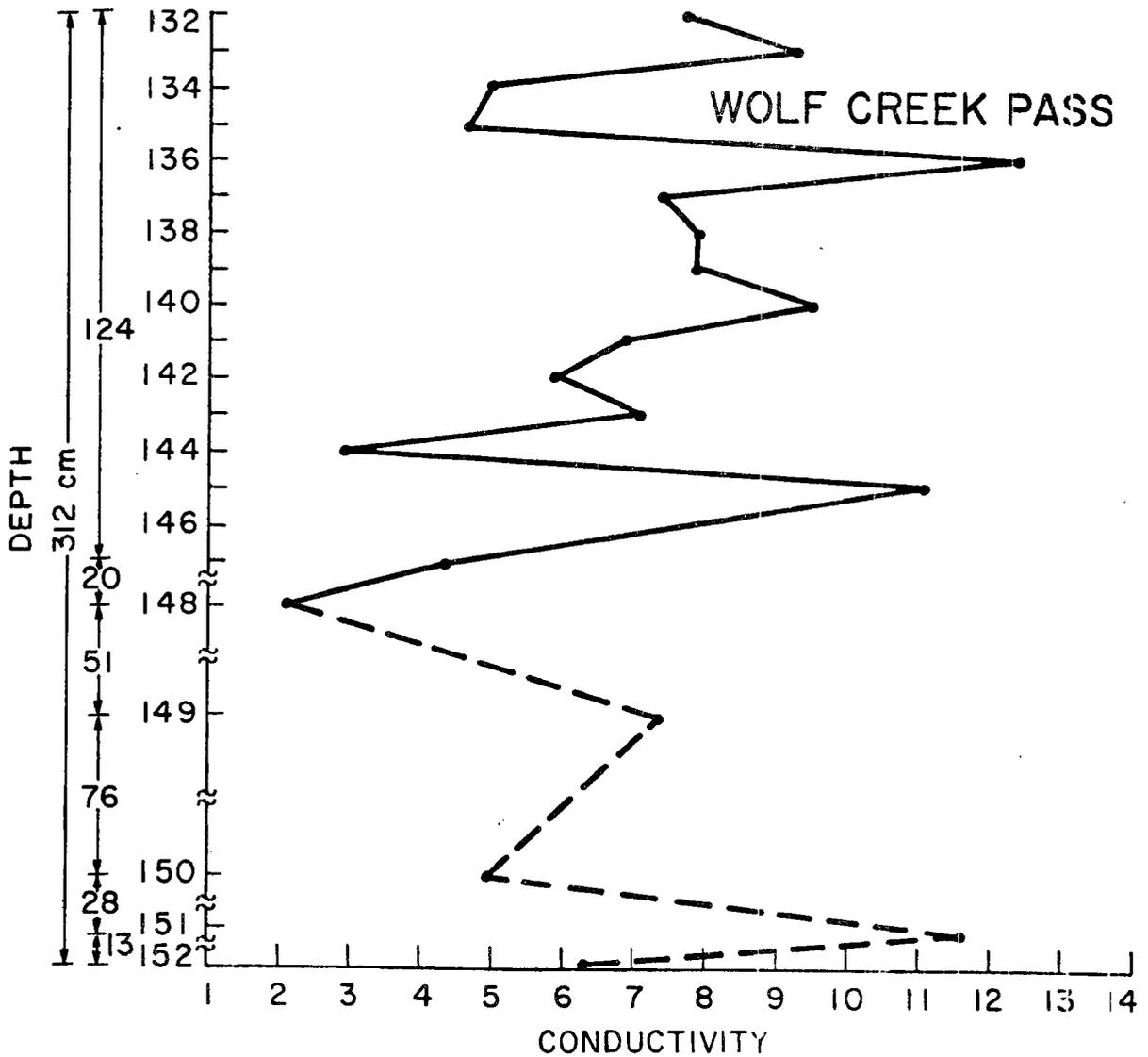


Figure 3.1b. Profile of specific conductivity within the snowpack for Wolf Creek Pass. The abscissa is marked in units of micromhos cm⁻¹ and the ordinate is marked according to sample number and depth, measured in centimeters. Dashed segments of the profile indicate that the sample at the midpoint of that segment was taken over the distance of that segment and represents the bulk conductivity value for the depth of the dashed segment.



Figure 3.2. Model precipitation pattern map for 210 degree flow (Rhea, 1978). Shaded areas represent areas of greater orographic enhancement.

the previous chapter, the pH profile at Wolf Creek Pass has wide variability. It would be expected that the lowest pH values would occur during southwesterly flow, while the higher values would occur from precipitation from other wind directions.

Rabbit Ears Pass: Of the five more polluted sites, snow from Rabbit Ears Pass (Figure 3.3a) has the most consistently low pH values. The median pH value at this site is 5.04. Ten of 21 samples have pH values less than 5.0. As seen in Figure 3.3a, the highest pH value at this site is only 5.51, almost neutral with respect to equilibrium with atmospheric CO₂, but still slightly on the acidic side. The lowest pH value found here was 4.70.

The conductivity values at this site are shown in Figure 3.3b; the median conductivity value was 7.07 micromhos cm⁻¹. The high conductivity value seen in this figure at number 54 is due to a layer of organic matter caused by the December drought, mentioned earlier.

The Rabbit Ears Pass site is located on the western edge of the Park Range, due east of the Hayden and Craig power plants. Rabbit Ears Pass is also the first barrier downwind from these plants during westerly flow. During northwesterly and southwesterly flow this site is in the precipitation shadow of other barriers (Figures 3.5 and 3.2). Being the first barrier to westerly flow, and receiving its highest amount of precipitation from westerly flow events (Figure 3.4), will enhance the effects of pollutants from the local upwind sources at this site. These two effects explain why the Rabbit Ears Pass site was the most consistently contaminated high elevation site.

Milner: The most outstanding feature of the pH profile of the Milner snowpit (Figure 3.6a) is that the top four samples show some variabil-

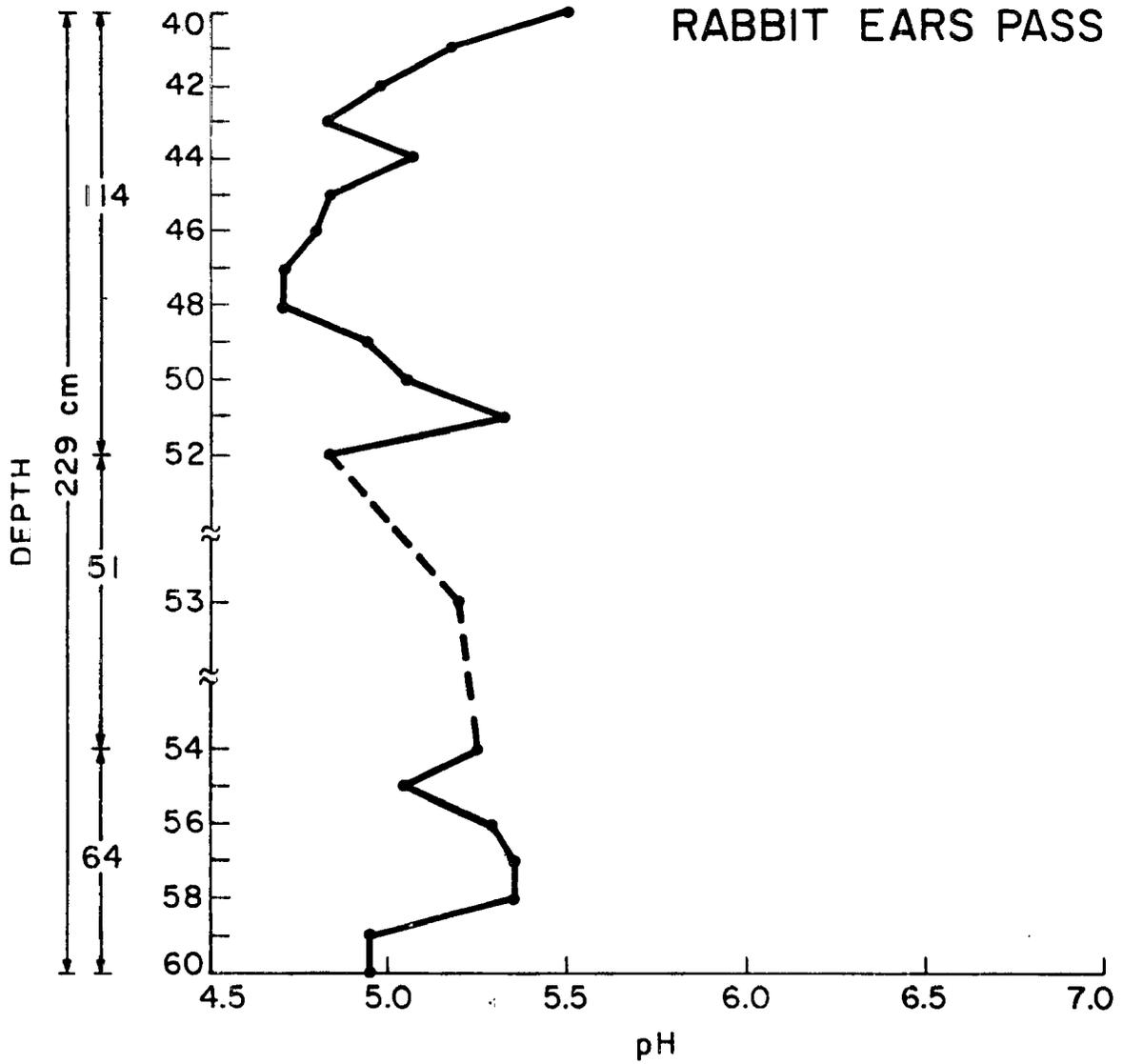


Figure 3.3a. Profile of pH within the snowpack for Rabbit Ears Pass.
Details the same as Figure 3.1a.

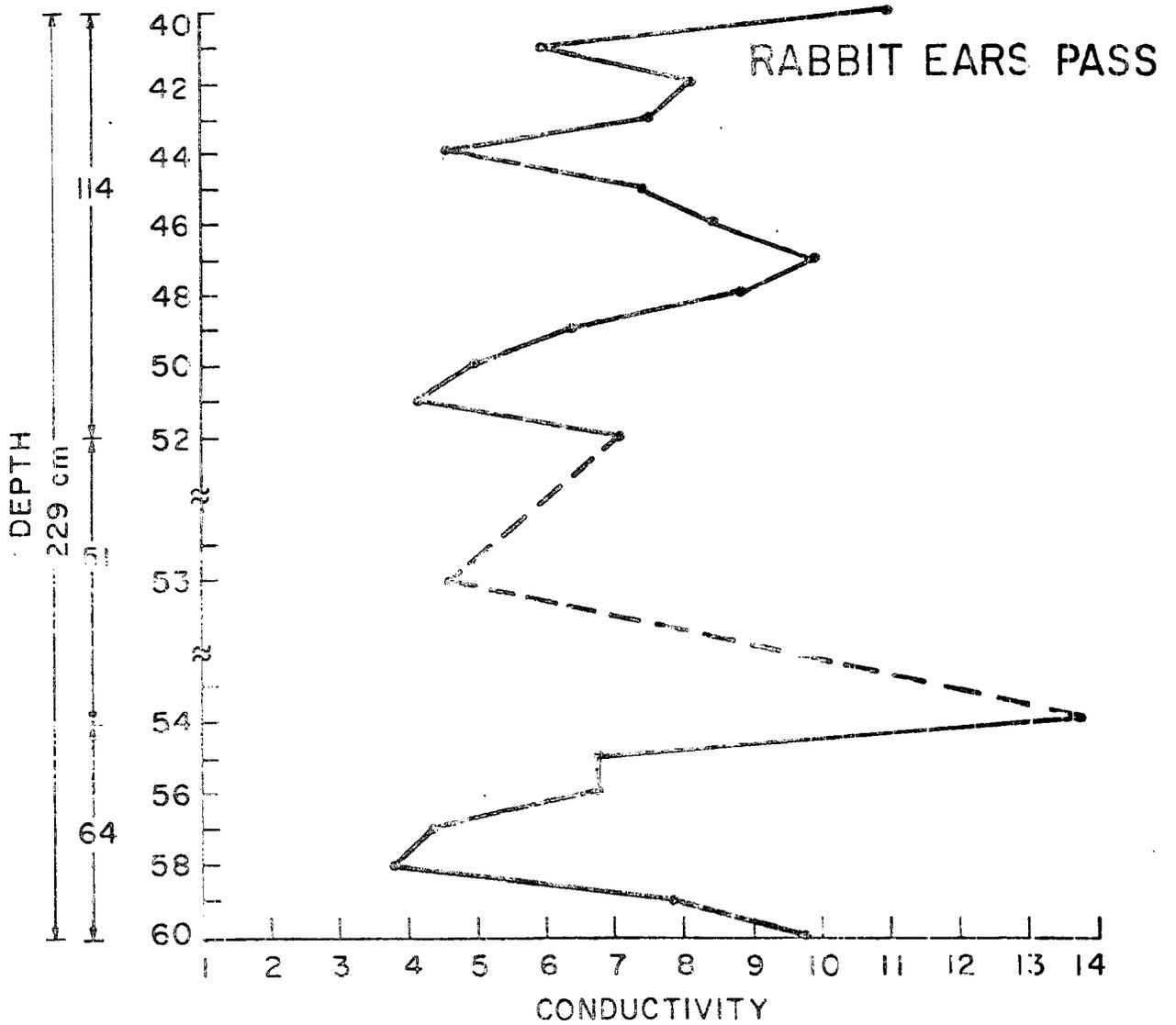


Figure 3.3b. Profile of specific conductivity within the snowpack at Rabbit Ears Pass. Details the same as Figure 3.1t.

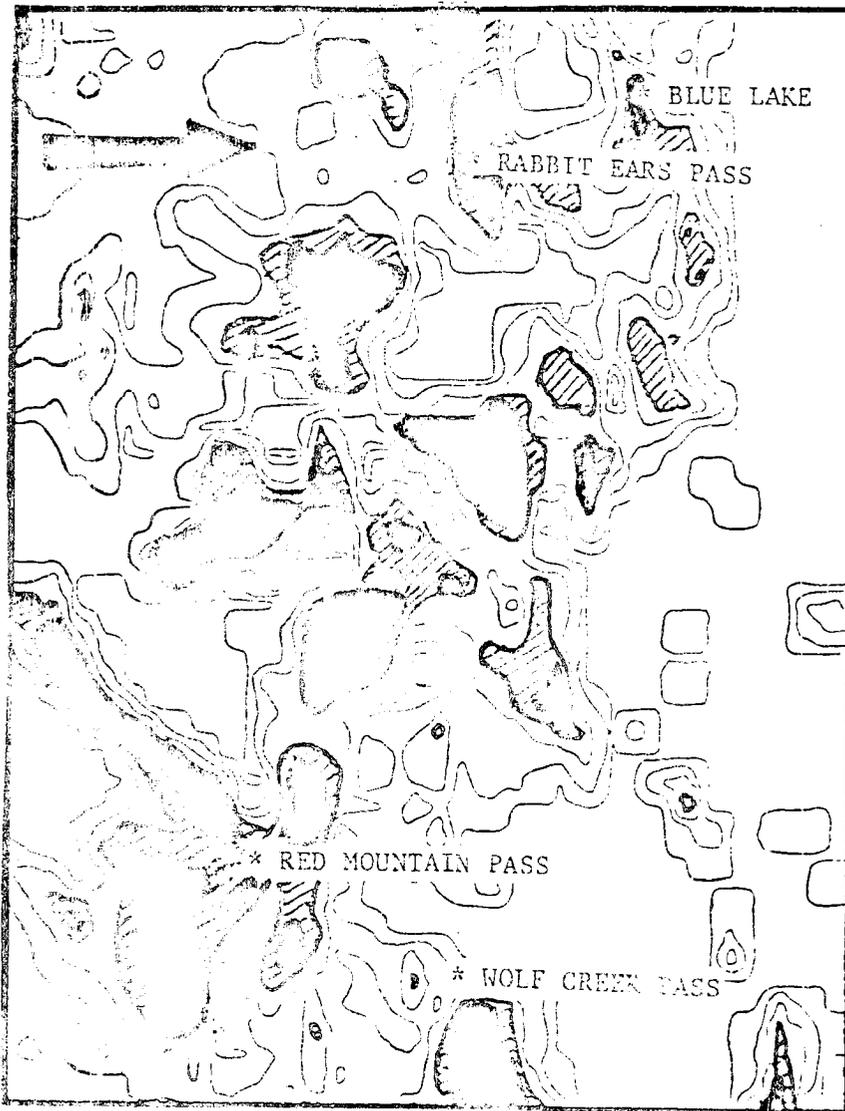


Figure 3.4. Model precipitation pattern map for 270 degree flow (Rhea, 1978). Shaded areas represent areas of greater orographic enhancement.

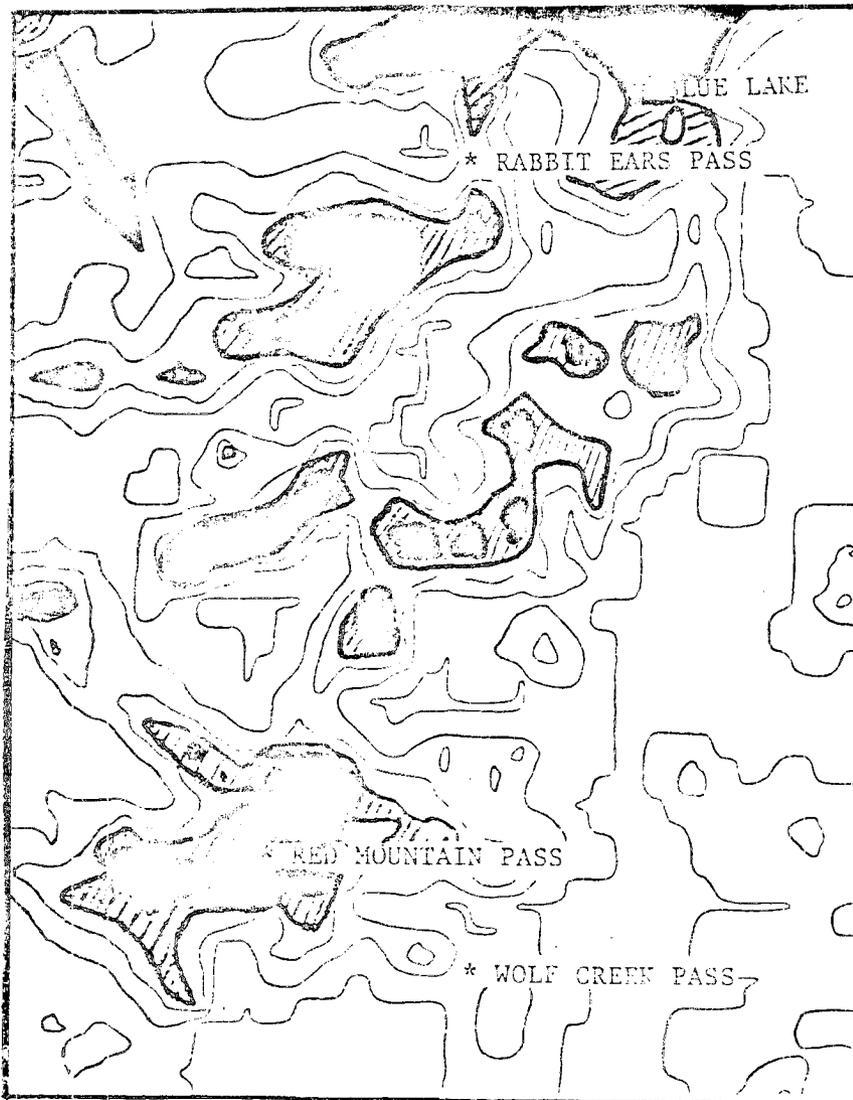


Figure 3.5. Model precipitation pattern map for 330 degree flow (Rhea, 1978). Shaded areas represent areas of greater orographic enhancement.

ity, then the remaining samples are fairly uniform in pH value. Because this was a valley site, the snowpack depth was only 91 cm. The median pH value at this site was 5.12. The conductivity profile (Figure 3.6b) shows the top four samples to have the highest conductivity values, followed by the lowest value, with the remainder of the samples' conductivity values falling in between these extremes. The median was 6.67 micromhos cm^{-1} .

The site at Milner was interesting for several reasons. One, its highest pH value was only 5.18. Secondly, the bottom six samples had essentially the same value. The generally low values were due to the close proximity of the Hayden power plant and a coal mine. The uniformity of the values of the lower samples is due to the elevation of the site. The previously mentioned sites are all at elevations greater than 2700 meters, this site is in the Yampa River Valley at an elevation of around 1800 meters. This leads to less snow on the ground and warmer ambient air temperatures. The combination of these factors apparently leads to some melt in the lower, older layers of the snowpack, allowing some percolation of liquid water to adjacent layers, which yields a more homogeneous distribution of hydrogen ions. The top four samples were from more recent snowfalls which had not yet undergone any melt. The presence of depth hoar in the lower layers at this site, as noted in chapter 2, indicates that although some melt has occurred, it has not been enough to runoff into the surface waters.

Blue Lake: The samples from the Blue Lake site show wider variability than those from Rabbit Ears Pass but less than those from Wolf Creek Pass. The median pH value falls to a value of 5.10, which is very similar to the median at Wolf Creek Pass. Figure 3.7a shows that the lowest

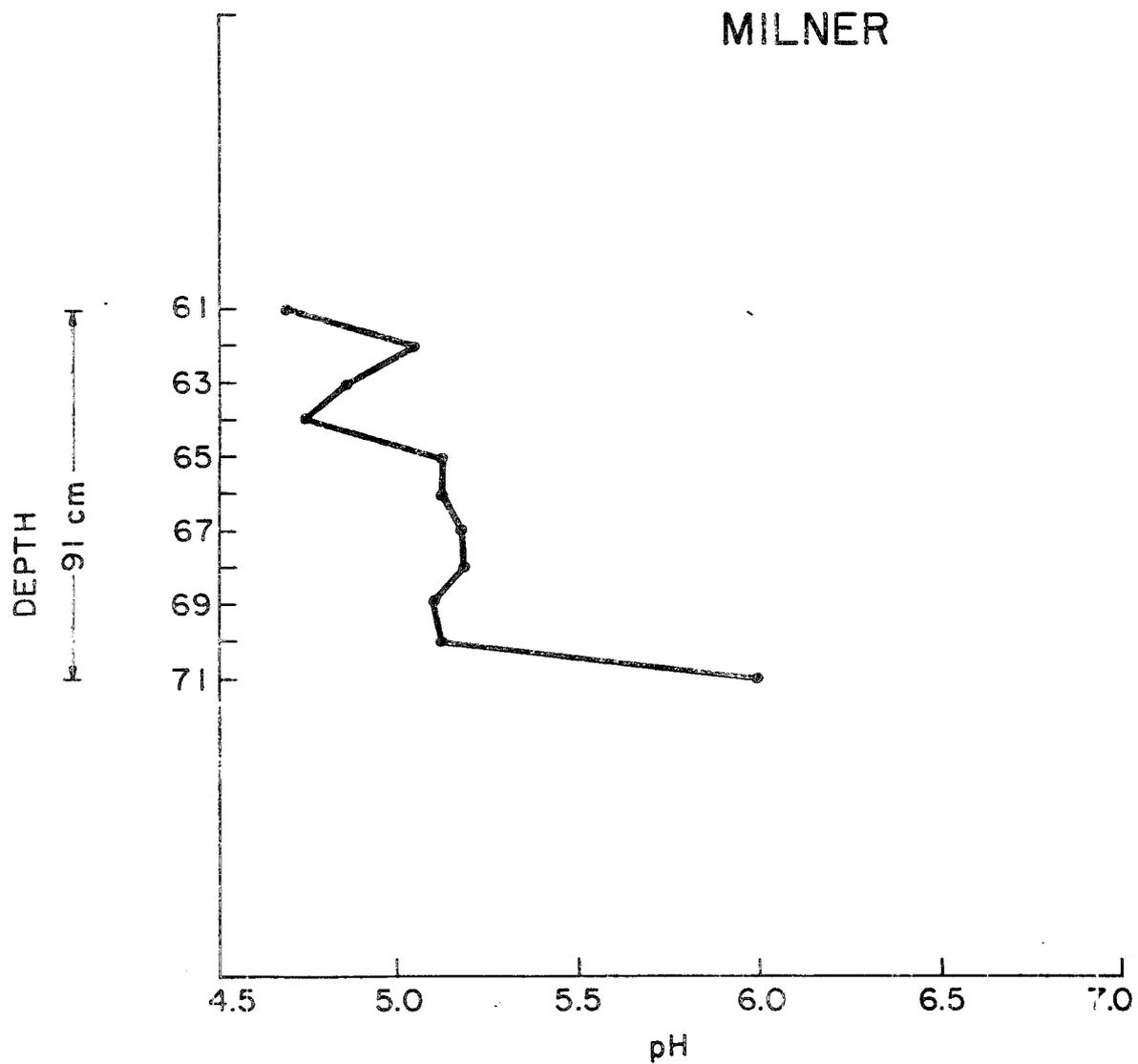


Figure 3.6a. Profile of pH within the snowpack for Milner. Details the same as Figure 3.1a.

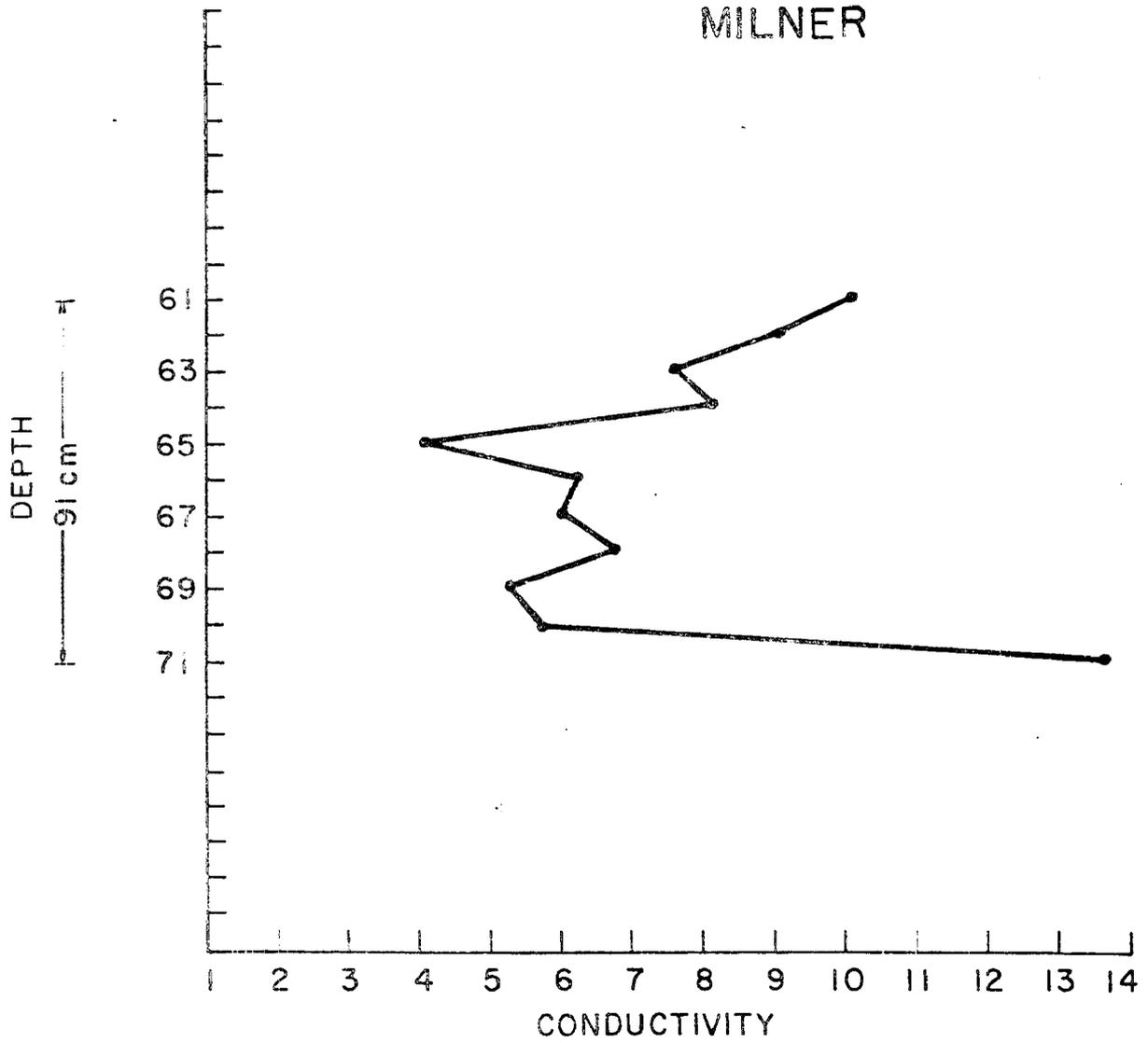


Figure 3.6b. Profile of specific conductivity within the snowpack at Milner. Details the same as Figure 3.1b.

pH value is only 4.92, a concentration almost one half of the lowest value at Wolf Creek Pass. The highest value is 5.99, the only value which is greater than 5.6, except for the bottom sample. The specific conductivity values at Blue Lake (Figure 3.7b) show less variability and lower absolute values than do either Wolf Creek or Rabbit Ears Pass. The median conductivity was only 4.46 micromhos cm^{-1} .

The Rabbit Ears Pass and Milner sites are in fairly close proximity to the power plants in the Yampa River Valley, and the power plants would appear to be the obvious sources for acidic pollutants. The Blue Lake site, however, is 105 km. and one more barrier to the east. The Blue Lake site had an acidic pH profile, the source of which cannot be explained readily in terms of a source in very close proximity. Orographic events which have the largest snowfall amounts at this site can come from the west, northwest, north or east. In terms of sources of acidic pollutants, the westerly flow or the easterly flow would be the most likely direction of transport. The westerly flow would carry acidic pollutants from the Yampa River Valley to this area from the high stacks at the power plants. With easterly flow, the nearest source of any acidic pollutants at the present time would be the Fort Collins area. The only source in Fort Collins would be automobile emissions. The site at Guanella Pass, discussed later, which is in a similar geographic situation in relation to the Front Range Urban Corridor, has high pH values in relation to the other sites and has no source of acidic pollutants to the west. The sources to the west should dominate the Blue Lake profile.

Long Lake: The site at Long Lake, just west of Boulder, near the continental divide, showed a pH profile similar to the first three dis-

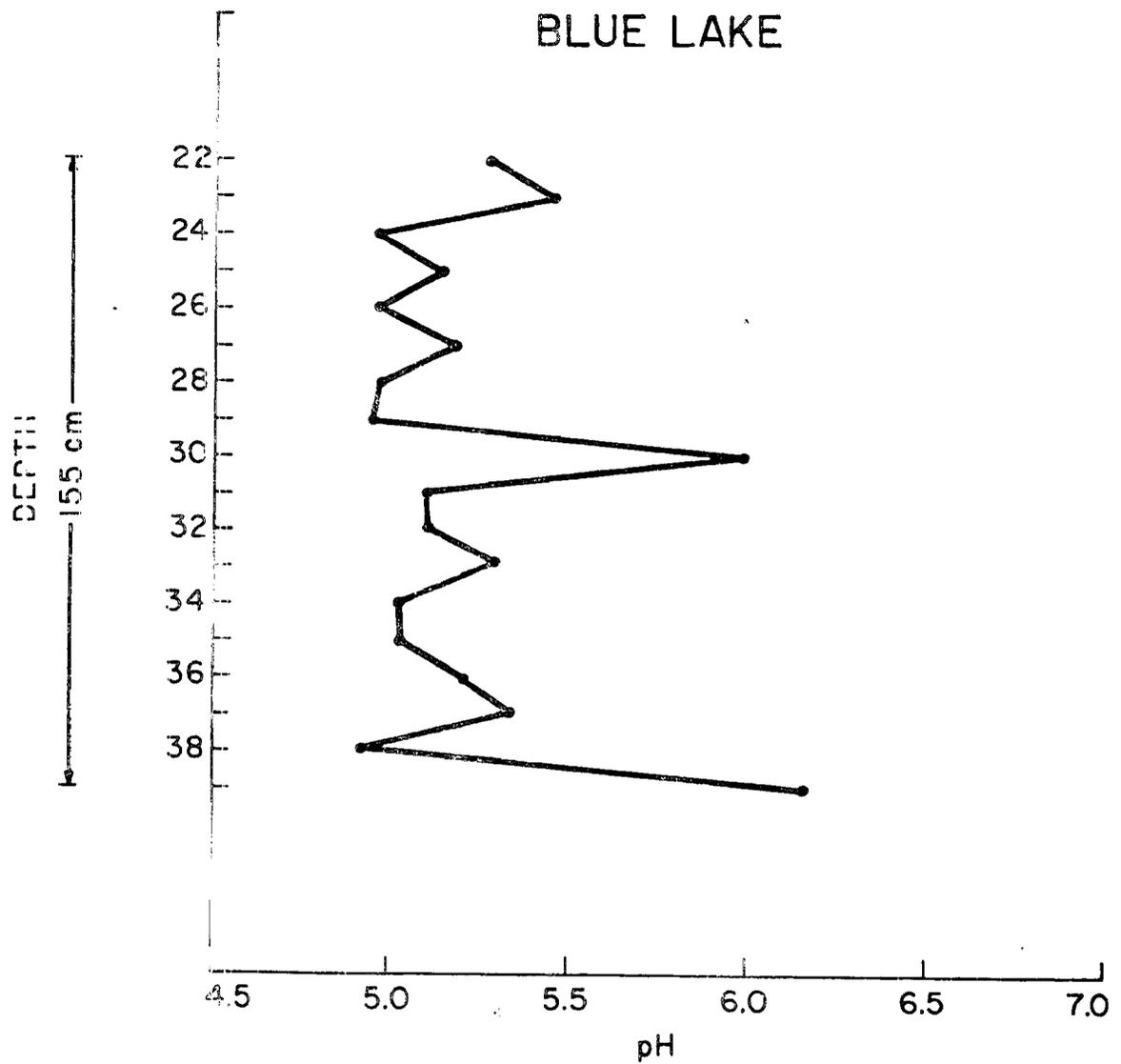


Figure 3.7a. Profile of pH within the snowpack for Blue Lake. Details the same as Figure 3.1a.

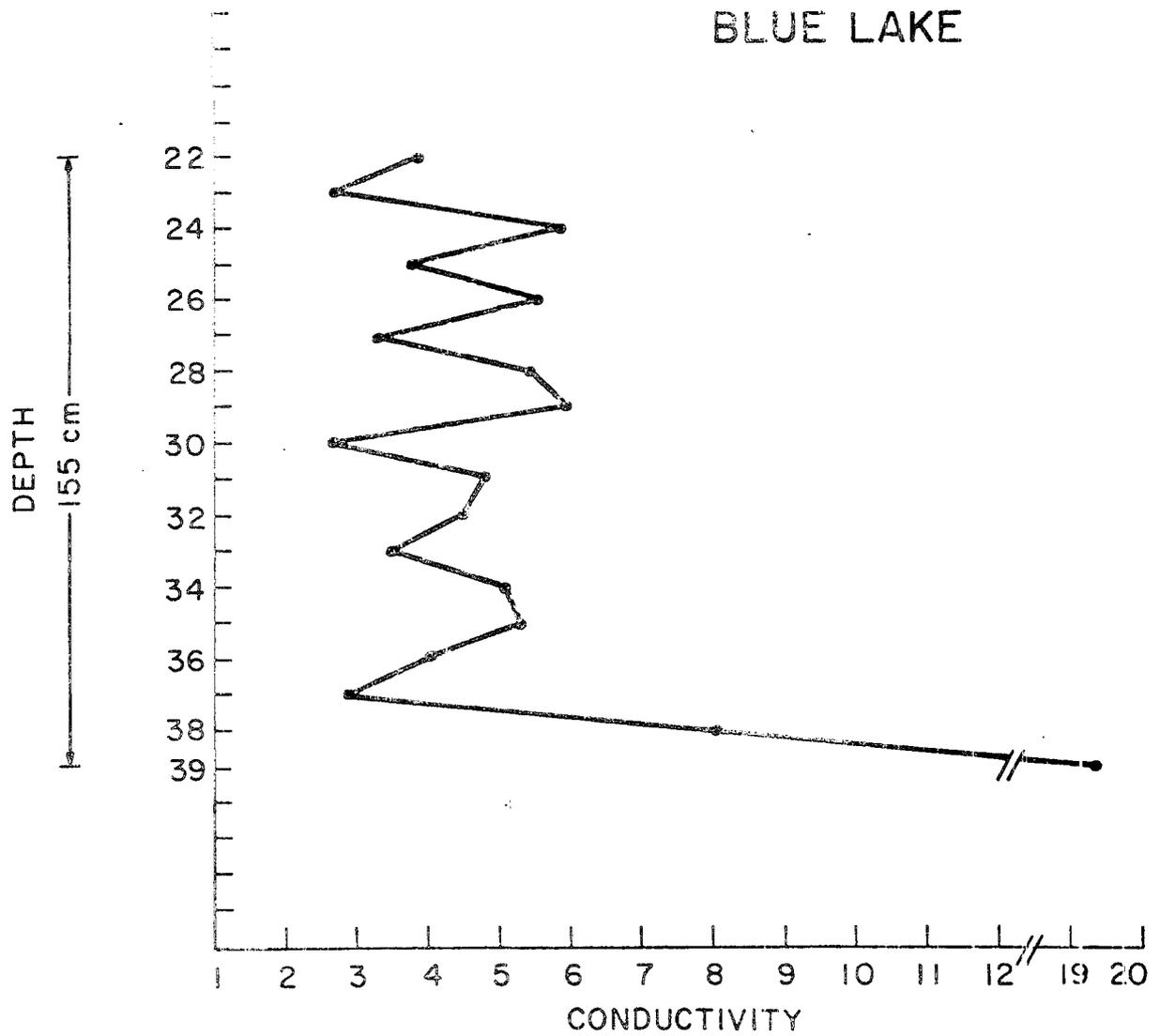


Figure 3.7b. Profile of specific conductivity within the snowpack at Blue Lake. Details the same as Figure 3.1b.

cussed (Figure 3.8a). The low value was 4.73 and the highest value was 5.49. The median value was 5.18. The specific conductivity profile at Long Lake (Figure 3.8b), exhibits values and variability similar to that at Rabbit Ears Pass, the median value is only 5.46 micromhos cm^{-1} .

There are no coal-fired power plants in the vicinity of Long Lake to affect the site, yet it still has an acidic pH profile. The Front Range Urban Corridor appears to be the source. The primary pollution problem in this area is NO_x from automobile emissions, which could lead to nitric acid formation in precipitation. This site is near to the Como Creek site used in the studies of Lewis and Grant (1980) and Kelly and Stedman (1980). As indicated by Kelly and Stedman (1980), concentrations of NO , NO_2 and HNO_3 were up to 100 times higher in periods of upslope air movement from the east than clean air movement from the west. Long Lake differs from Guanella Pass, a "clean" site, and Blue Lake in that it is much closer to the urbanized areas with fewer topographic features in between and is therefore affected by pollutant transport from the east. Sources to the west would be similar to Guanella Pass. These facts support the urbanization to the east as the source of acidic precipitation found at this site.

McClure Pass: The previous sites mentioned were those which showed some effects of contamination. This site is the first to be discussed which appears to be predominantly free from such effects. The pH values at McClure Pass ranged from 4.85 to 6.85, as seen in Figure 3.9a. The range of values at this site is not too different from the more polluted sites, however, only two samples had pH values which fell lower than 5.0, while eight of the samples had pH values near or greater than 5.6. The median pH value at this site was 5.35.

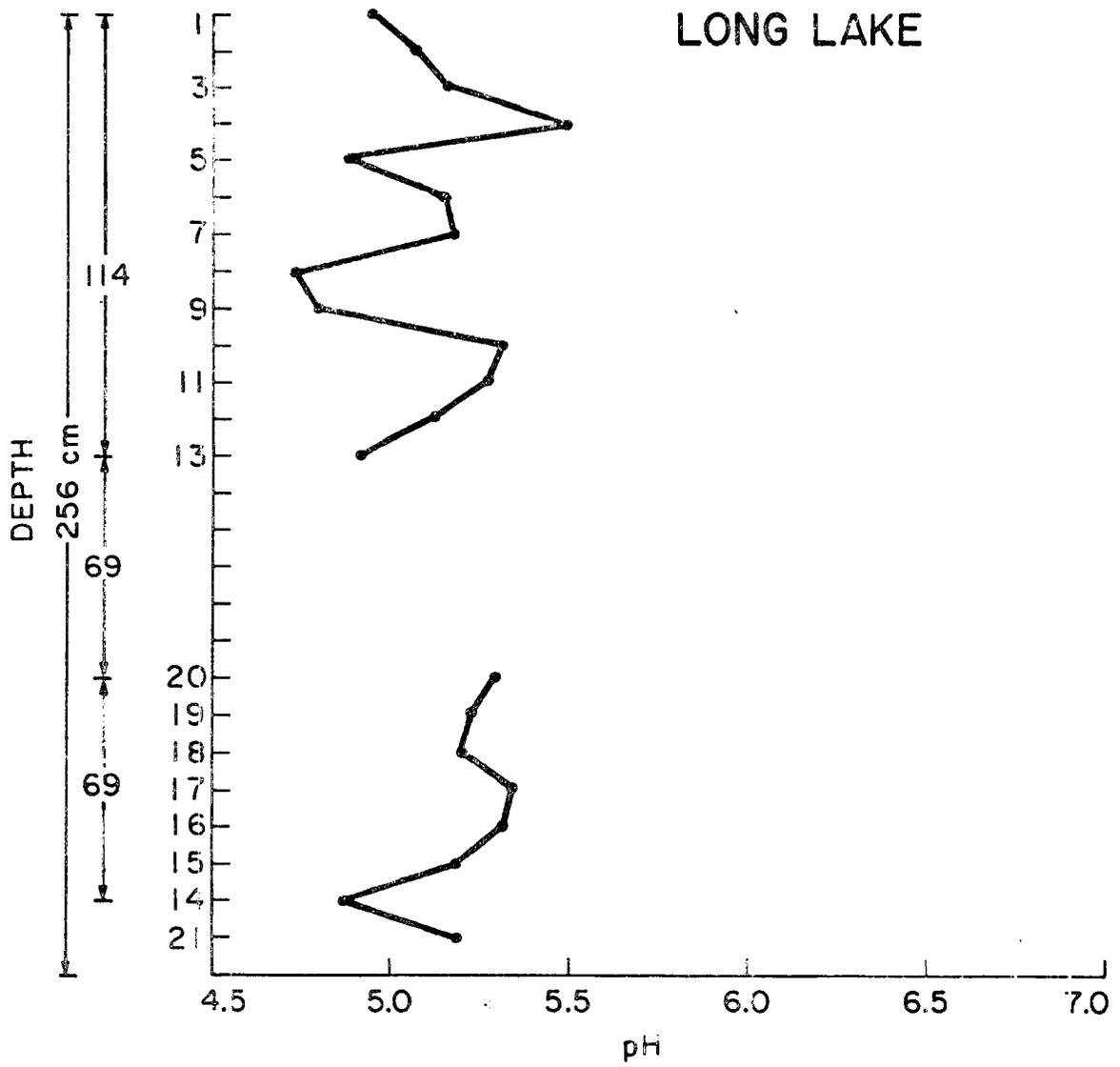


Figure 3.8a. Profile of pH within the snowpack for Long Lake. Details the same as Figure 3.1a.

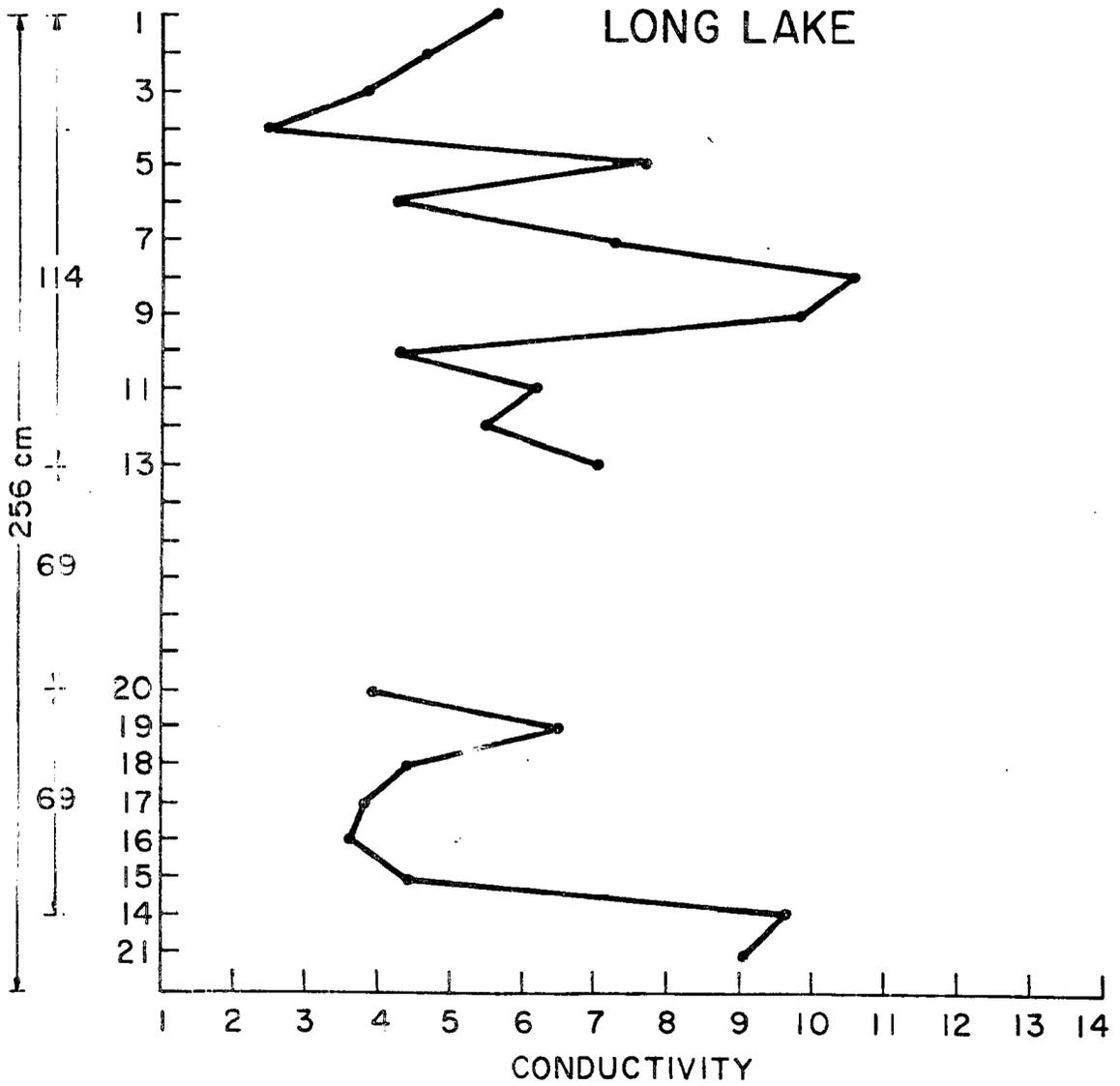


Figure 3.8b. Profile of specific conductivity within the snowpack at Long Lake. Details the same as Figure 3.1b.

The conductivity profile (Figure 3.9b) at McClure Pass is variable, as were the previously mentioned profiles. At McClure Pass, however, the general conductivity values were lower. The previously mentioned sites had median conductivity values between 4.46 at Blue Lake and 7.32 at Wolf Creek Pass, while the median conductivity at McClure Pass is only 3.75 micromhos cm^{-1} .

McClure Pass is on the western side of the Rockies and essentially on the first barrier to westerly flow. The only major population center near this site is Grand Junction, to the west. This has no industries or activities which are likely to contribute acidic pollutants to this site, other than automobile emissions.

Climax: At Climax, the samples collected showed the least variability overall. The median value at this site was 5.39. All but three samples had pH values which fell within one quarter of a pH unit from the median. The lowest value at Climax was 5.15 and the highest was 6.75 (Figure 3.10a).

The values of the conductivity profile from Climax (Figure 3.10b) were much lower than at the other sites. The median conductivity value at Climax was 3.16, the lowest of any of the sites.

The site at Climax is in the interior of the state. From any direction of air flow, this site will have numerous mountain barriers upwind of it, allowing most any acidic contaminants to be washed out before they reach this site. This is evidenced by the fact that this was relatively the "cleanest" site overall.

Guanella Pass: The samples from Guanella Pass ranged from 5.00 to 6.68, with a median value of 5.41. This site was very near to timberline and had undergone much modification from the wind, negating the assumption,

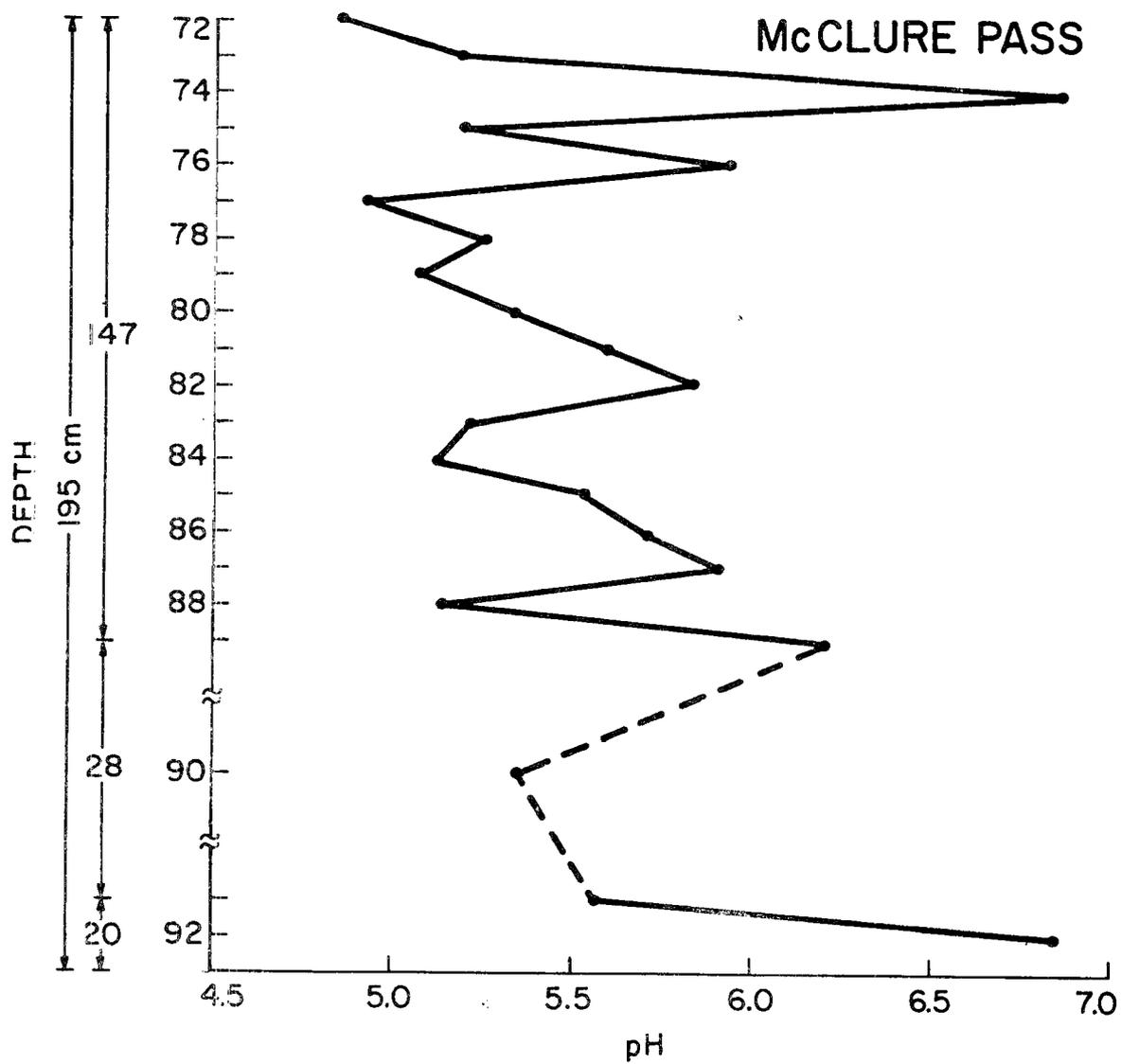


Figure 3.9a. Profile of pH within the snowpack for McClure Pass.
 Details the same as Figure 3.1a.

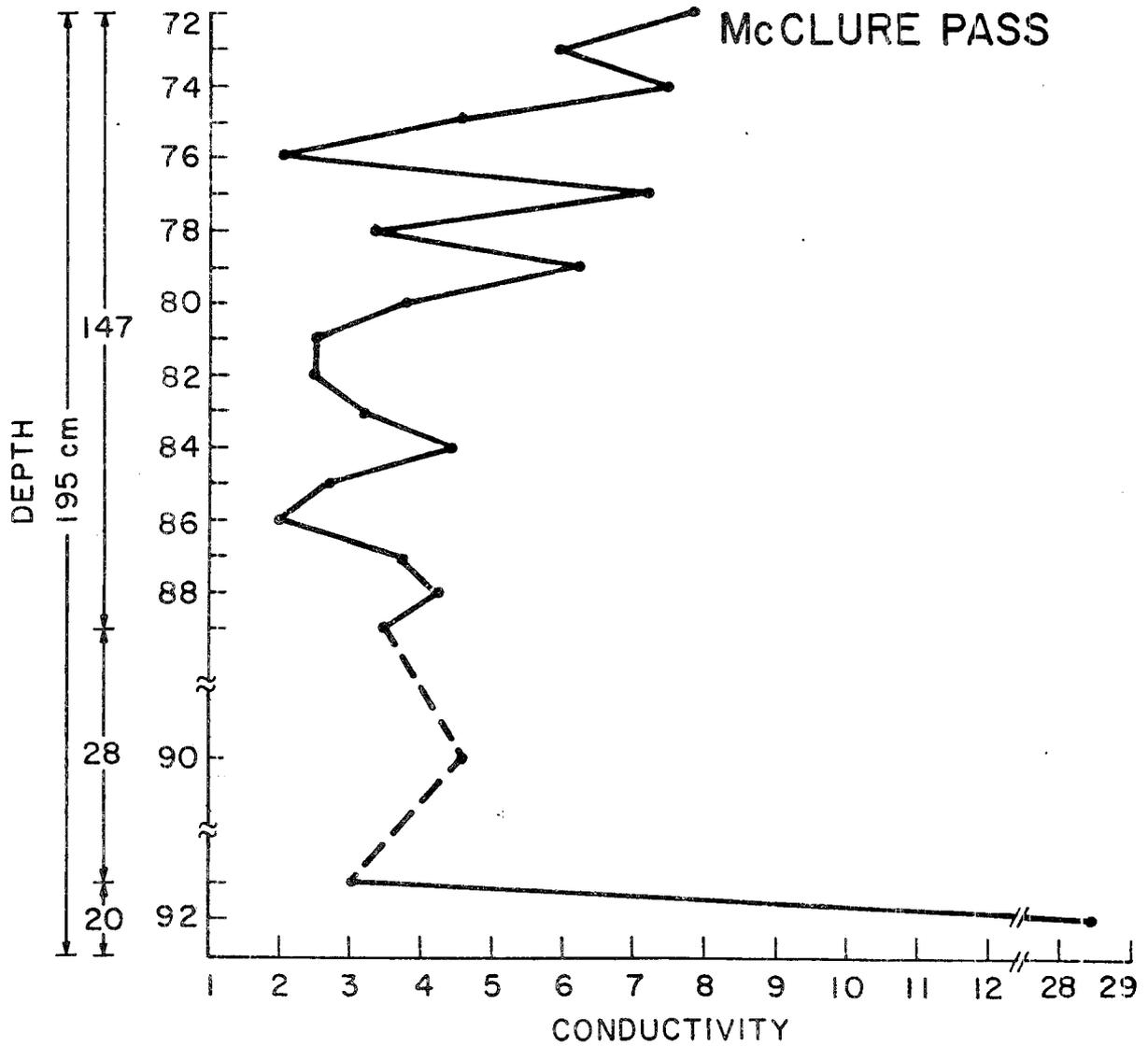


Figure 3.9b. Profile of specific conductivity within the snowpack at McClure Pass. Details the same as Figure 3.1b.

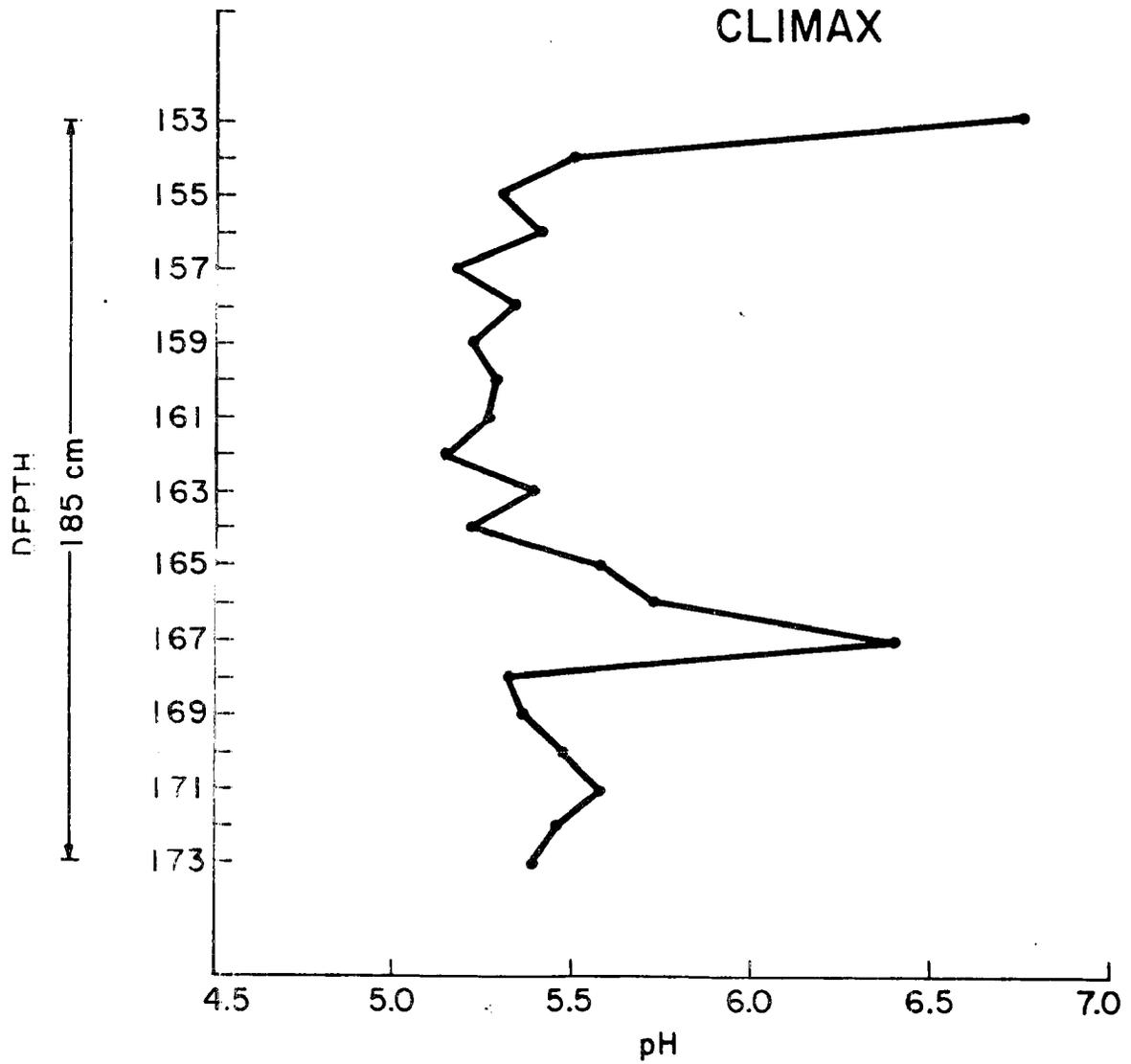


Figure 3.10a. Profile of pH within the snowpack for Climax. Details the same as Figure 3.1a.

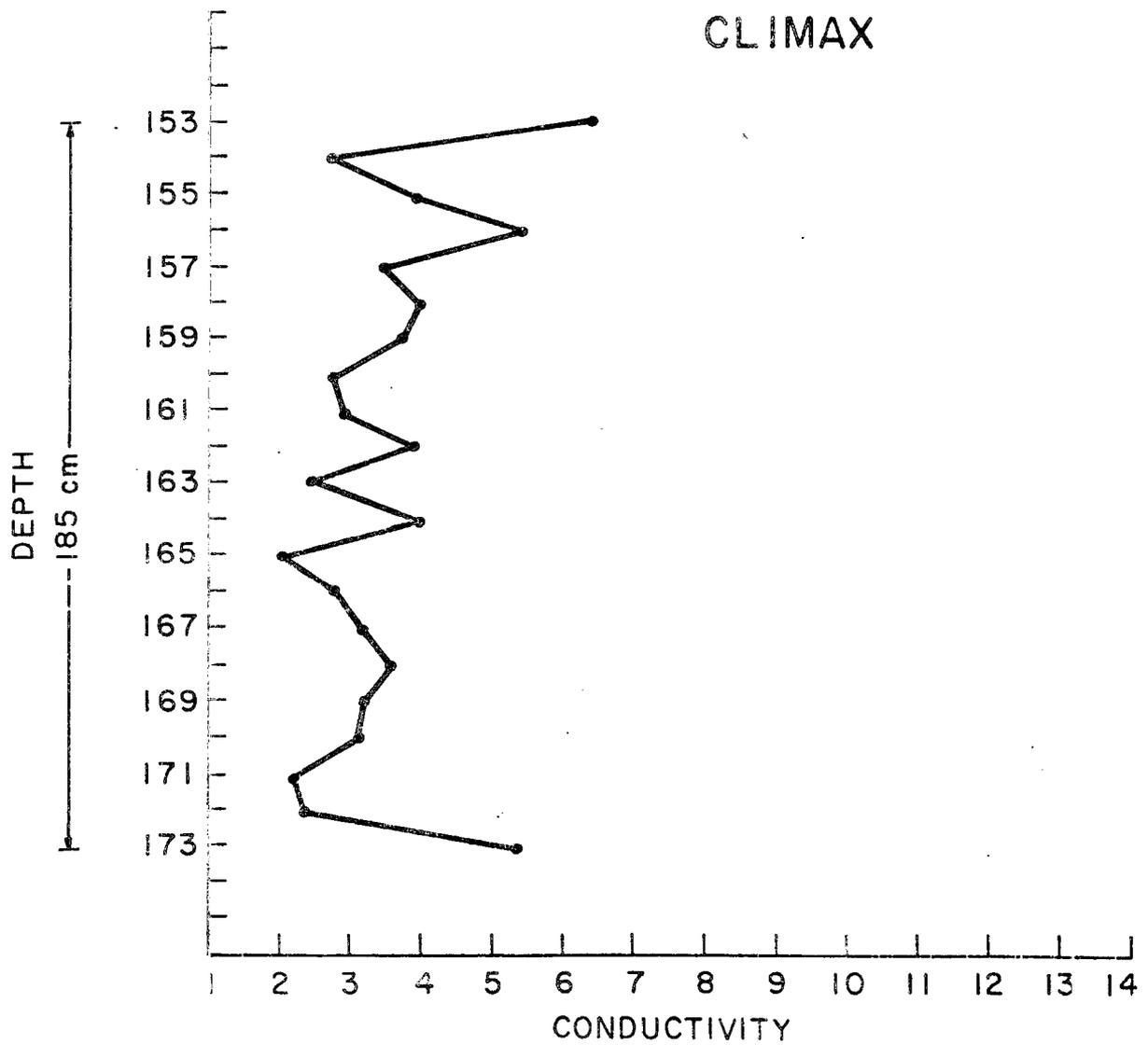


Figure 3.10b. Profile of specific conductivity within the snowpack at Climax. Details the same as Figure 3.1b.

valid at the other sites, that it would be a contiguous representation of the precipitation which fell at that site (Figure 3.11a). The conductivity values of the samples from this site are all relatively low (Figure 3.11b). The median value is $4.33 \text{ micromhos cm}^{-1}$.

The site at Guanella Pass is geographically similar to Blue Lake, mentioned earlier. There are about 65 km. of foothills and mountains between this site and the extensive urbanization at the base of the mountains. Any pollutants moving upslope, from the east, could be washed out before this site. As well as this, there is a high ridge to the east of the site, in excess of 4000 meters, which shadows precipitation at this site from easterly flow.

Red Mountain Pass: Red Mountain Pass, even though in close proximity to Wolf Creek Pass, was one of the cleaner sites. The median pH value was 5.47. The range of pH values is similar to Wolf Creek Pass, 4.70 to 6.63, but there are more samples with pH values greater than 5.6, eight versus five at Wolf Creek, and 11 samples with pH values less than 5.1 at Wolf Creek while Red Mountain only shows six (Figure 3.12a). There are some higher conductivity values at Red Mountain Pass, but many were relatively low (Figure 3.12b). The median value is $3.99 \text{ micromhos cm}^{-1}$.

Red Mountain Pass is in close proximity to Wolf Creek Pass. Even though this is to the NNE of the Four Corners Power Plant, it does not have the markedly acidic profile that Wolf Creek Pass has. This is because this site is in the precipitation shadow of the southern San Juan Mountains during a southwesterly flow pattern (Figure 3.2). This site will receive most of its snow from flow with northerly component of flow (Figure 3.5), which has no consistent sources of acidic pollutants.

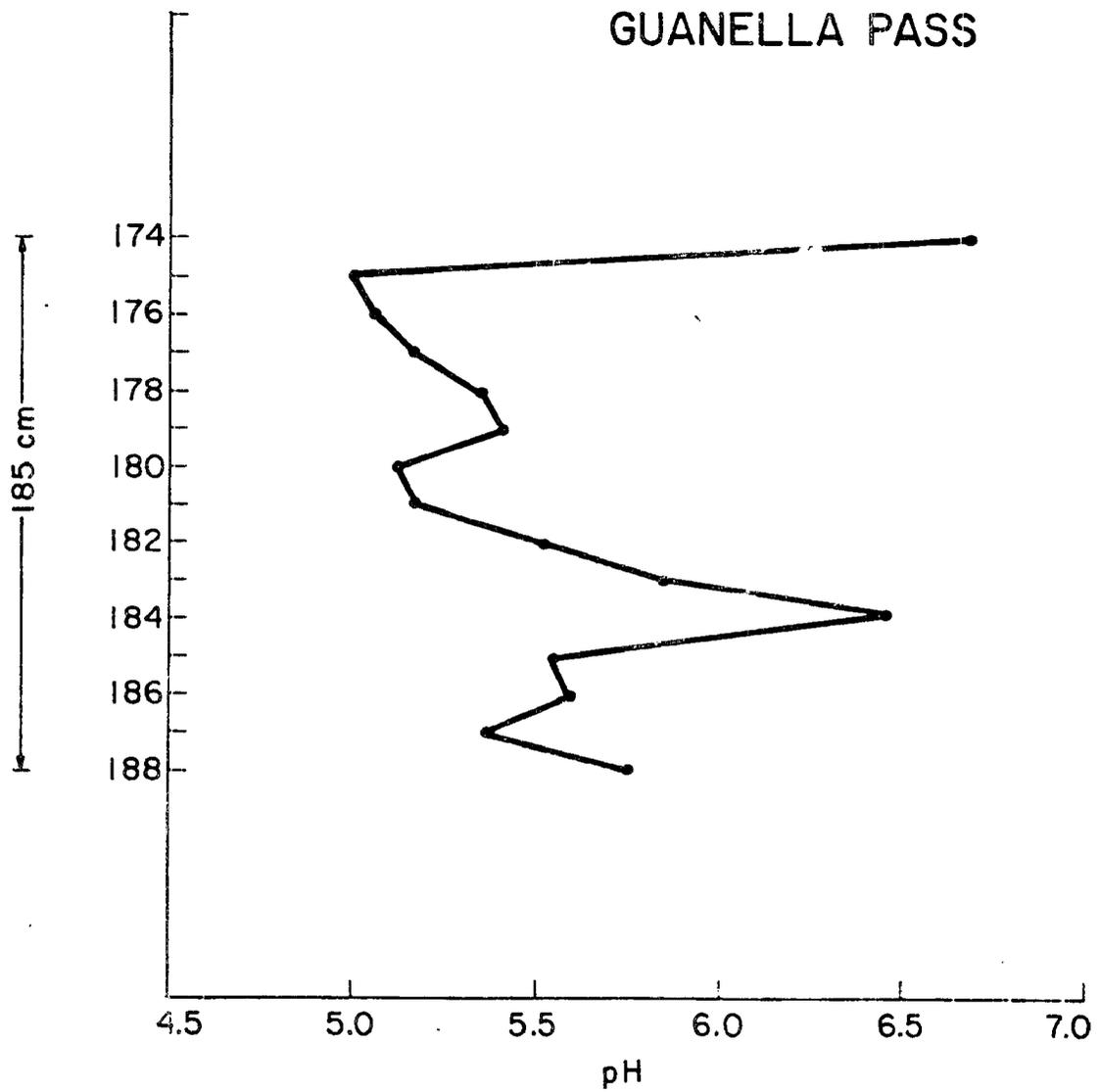


Figure 3.11a. Profile of pH within the snowpack for Guanella Pass.
Details the same as Figure 3.1a.

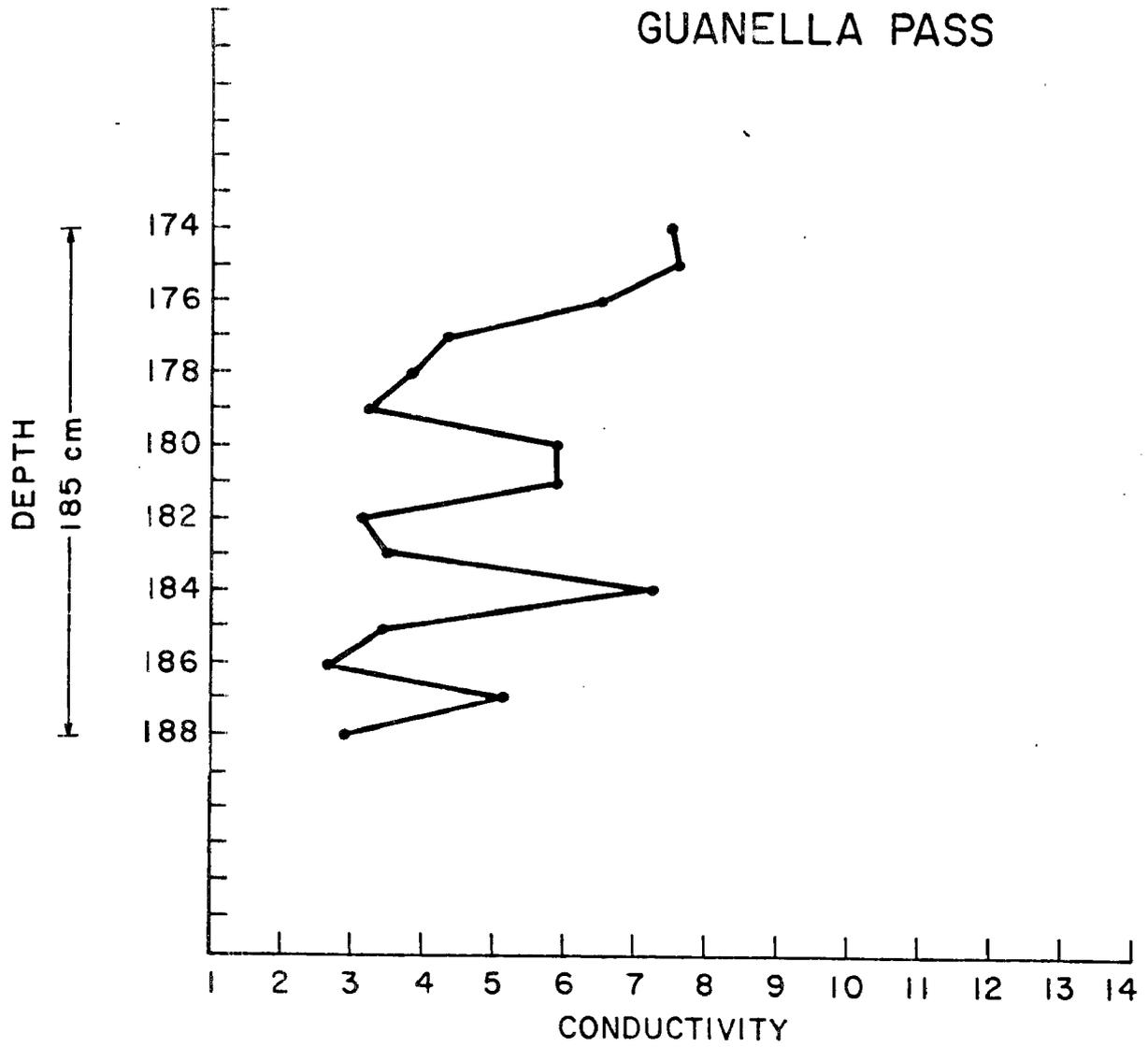


Figure 3.11b. Profile of specific conductivity within the snowpack at Guanella Pass. Details the same as Figure 3.1b.

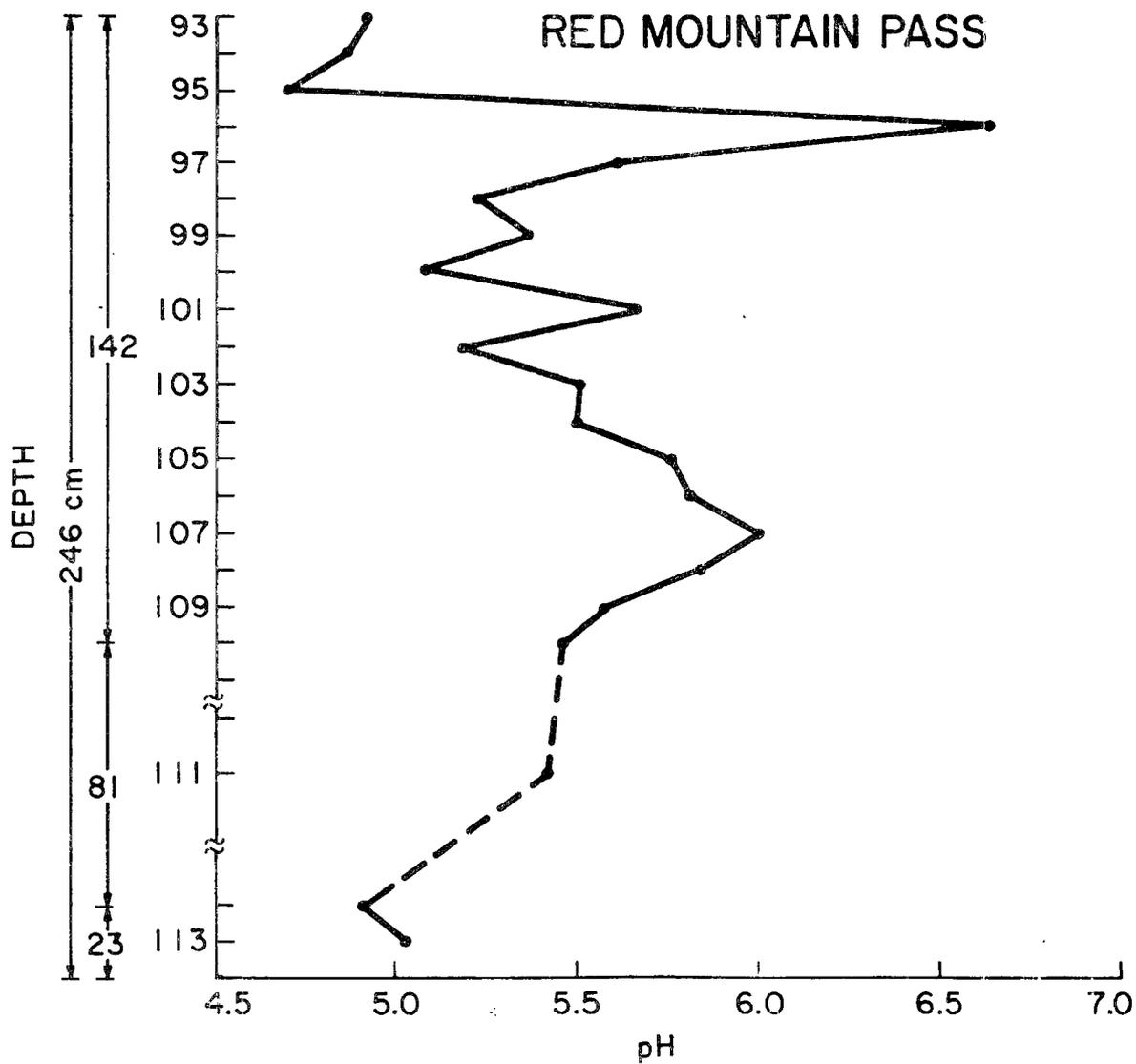


Figure 3.12a. Profile of pH within the snowpack for Red Mountain Pass. Details the same as Figure 3.1a.

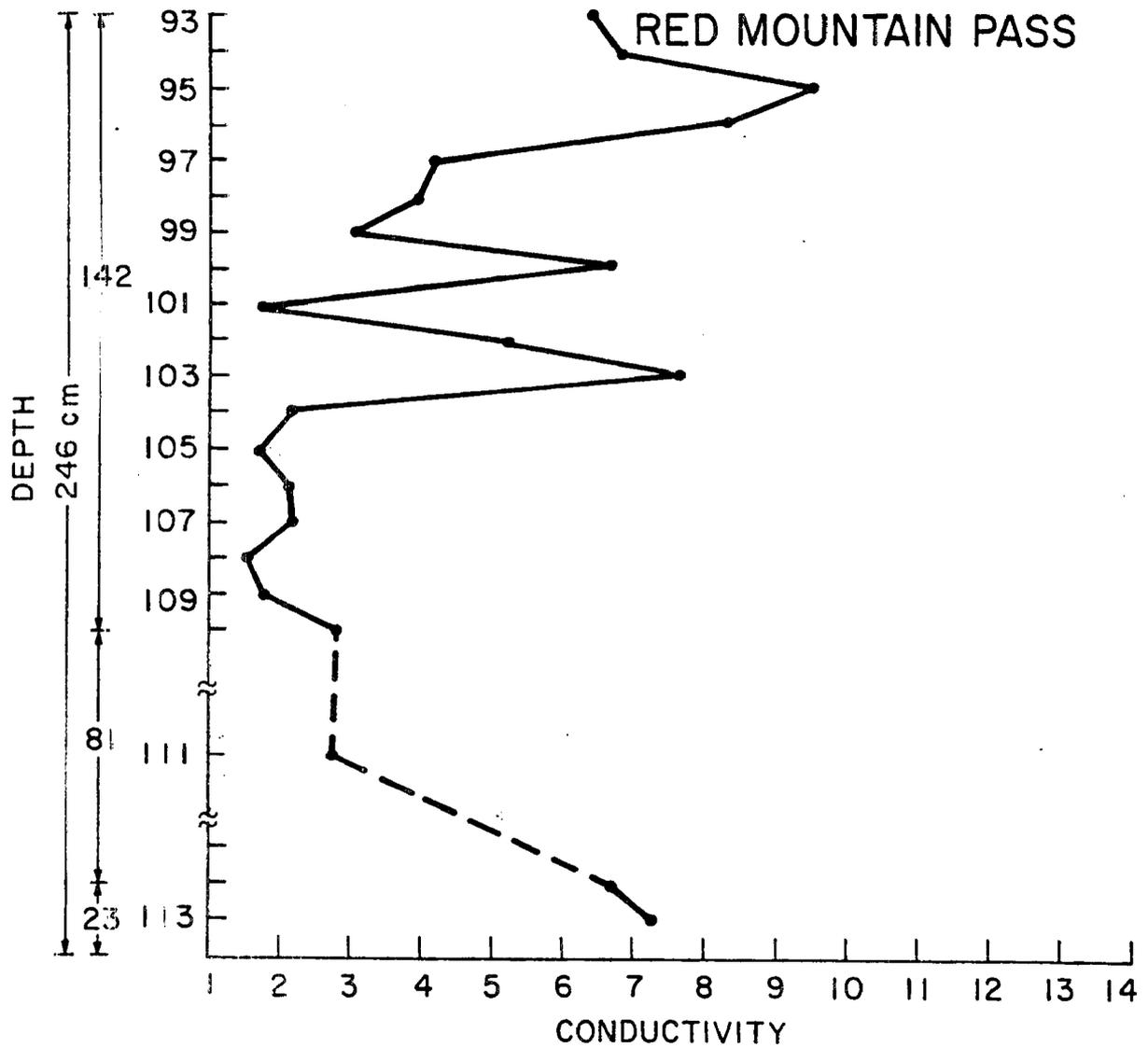


Figure 3.12b. Profile of specific conductivity within the snowpack at Red Mountain Pass. Details the same as Figure 3.1b.

Miscellaneous Data: As well as the above snowpits, some miscellaneous data was collected, including some from a second snowpit at Red Mountain Pass. This data is found in Appendix A.

Statistical Comparison of pH Between Sites

Sites were compared statistically with each other using the Wilcoxon two sample test. The null hypothesis used was that there were no differences between the pH values from different sites. A normal distribution is assumed and the two tail test of probability is used. A probability of 10% or less of observing the pH differences by chance is used to invalidate the null hypothesis.

The first comparison was between McClure Pass and each of the other mountain sites, taken individually. The McClure Pass pH profile is thought to represent the amount of acid being transported into the state. The probability of observing by chance the difference in pH values between either Long Lake, Blue Lake, Rabbit Ears Pass or Wolf Creek Pass and McClure Pass is less than 4% in each case. The probability for either Red Mountain Pass, Climax, or Guanella Pass for the same comparison, is between 60 and 90%, depending on the individual site. Hence, the former four sites are statistically different from McClure Pass and the latter three are not statistically distinguishable from McClure Pass.

Other comparisons were also made. When Long Lake was compared with Blue Lake and Rabbit Ears Pass, a difference could not be distinguished. When compared with Guanella Pass, the observed differences only had a 0.04% probability of occurring by chance. When Rabbit Ears Pass was compared with Blue Lake, there was a 14% probability that the differences occurred by chance, indicating that it can not be ruled out that

they are the same. The difference between Wolf Creek and Rabbit Ears Pass had a 59% probability of occurring by chance. Using the 10% probability confidence level, Wolf Creek Pass was not distinguishable from Red Mountain Pass. The probability that the differences between these two sites occurred by chance is only 10.5%, only barely beyond the cutoff confidence level. Climax and Guanella Pass were also statistically indistinguishable.

3.2 May 1980 Sampling Period

Samples were again collected at Blue Lake and Rabbit Ears Pass during May 1980, to indicate the effect of spring melt on the ionic content of the snowpack. Figures 3.13a and 3.13b show the pH and conductivity profiles for Rabbit Ears Pass from this sampling period. The most notable feature of this pH profile is the reduction of the number of low pH values. Only one sample value falls below a pH of 5.0 and the median value has increased to 5.39. The conductivity values are reduced also.

The profiles of pH and conductivity from Blue Lake, shown in Figures 3.14a and 3.14b, also show significantly reduced values of conductivity and acidity. In Figure 3.14a it should be noted that the pH at sample number 226 is similar in value to sample number 30, collected earlier, shown in Figure 3.7a.

The snowpit samples obtained in May 1980 at Rabbit Ears Pass and Blue Lake show the effect of the spring melt on the ionic content of the Colorado snowpack. The difference in these two sites is the depth of the snowpack and hence, the relative amount of melt which has taken place. Both profiles show some variability. At the Rabbit Ears site this variability extends throughout the depth of the snowpack, while the Blue Lake profile shows variability near the top of the snowpack and

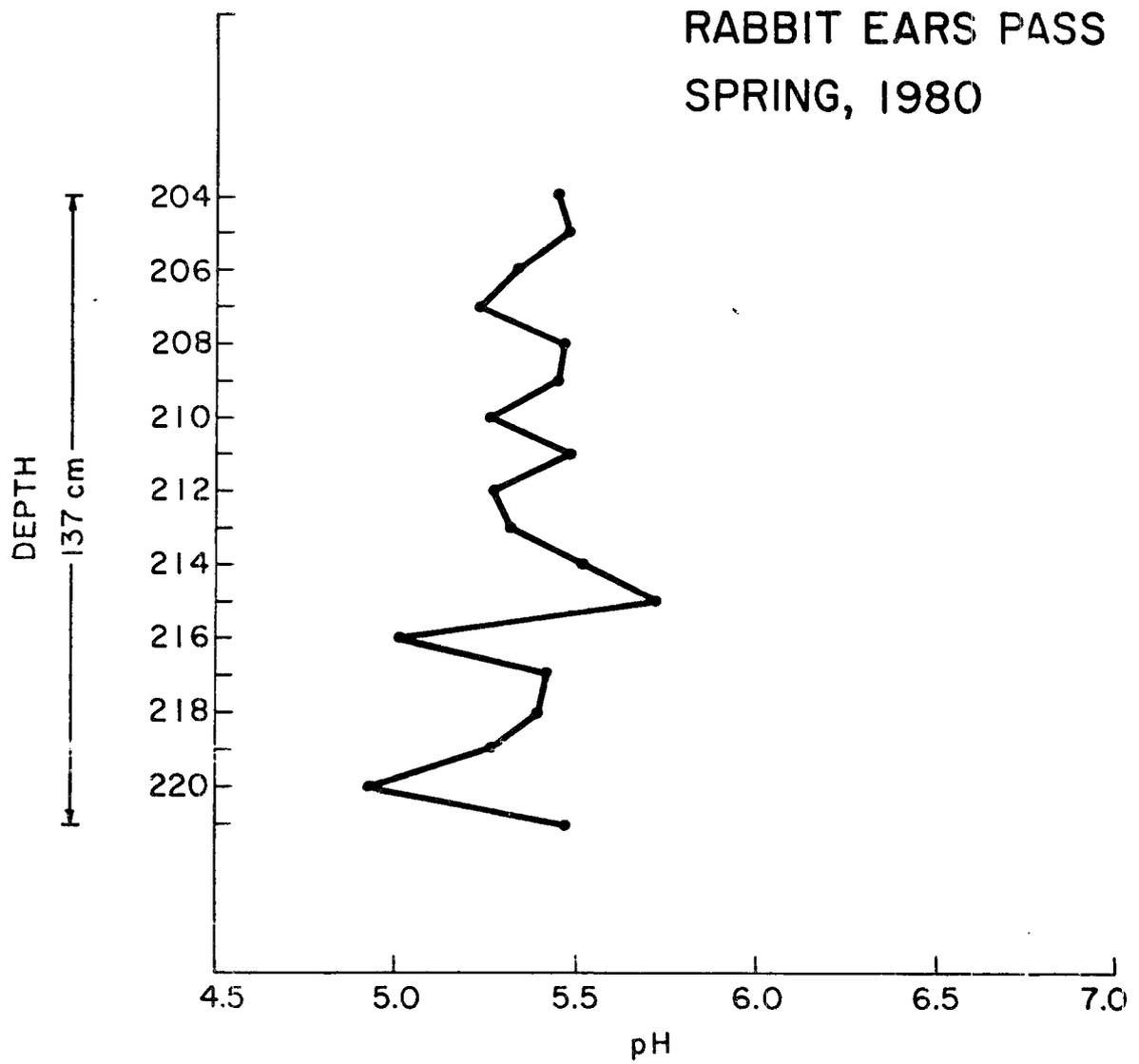


Figure 3.13a. Profile of pH within the snowpack for Rabbit Ears Pass, spring 1980. Details the same as Figure 3.1a.

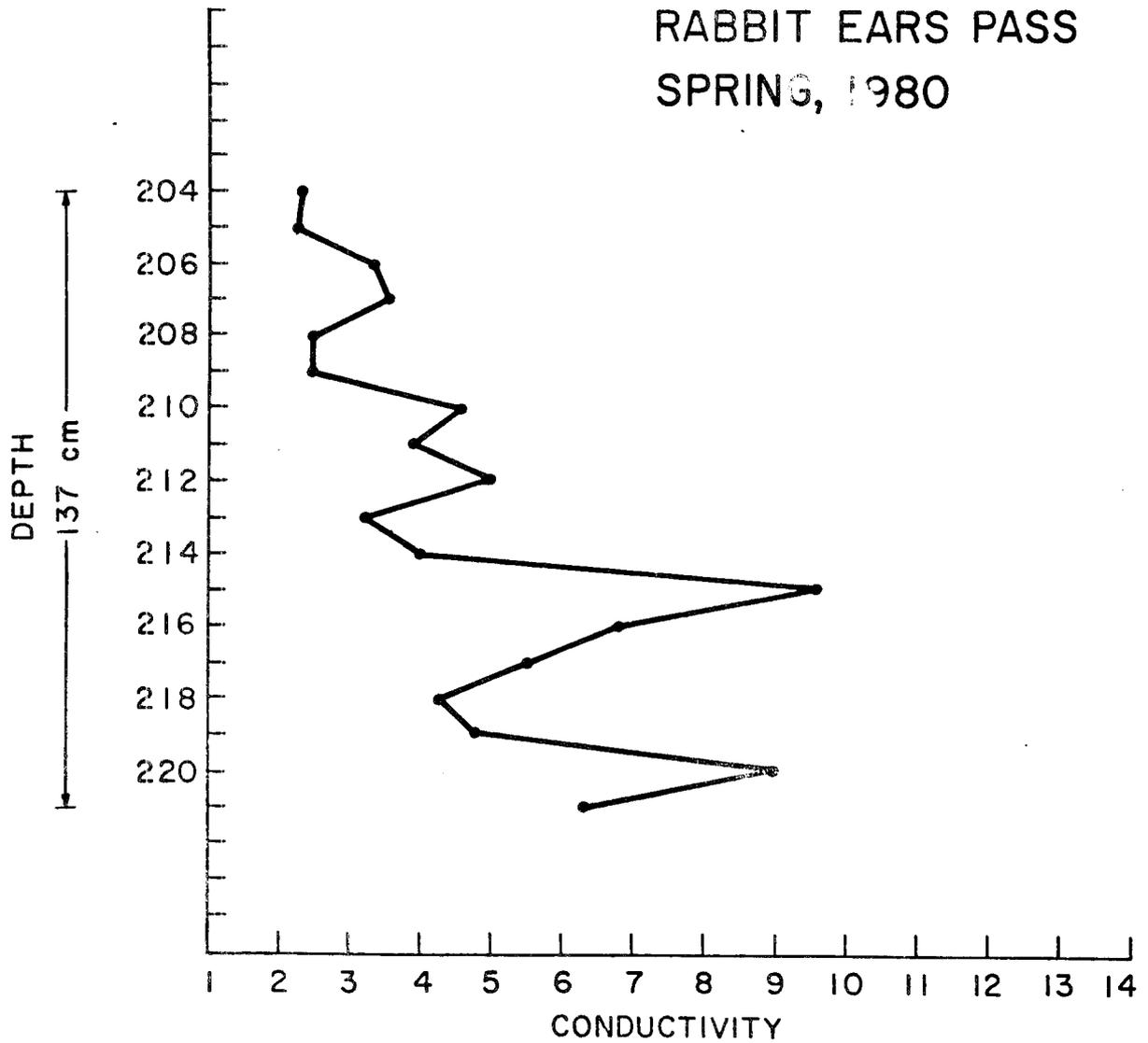


Figure 3.13b. Profile of specific conductivity within the snowpack at Rabbit Ears Pass, spring 1980. Details the same as Figure 3.1b.

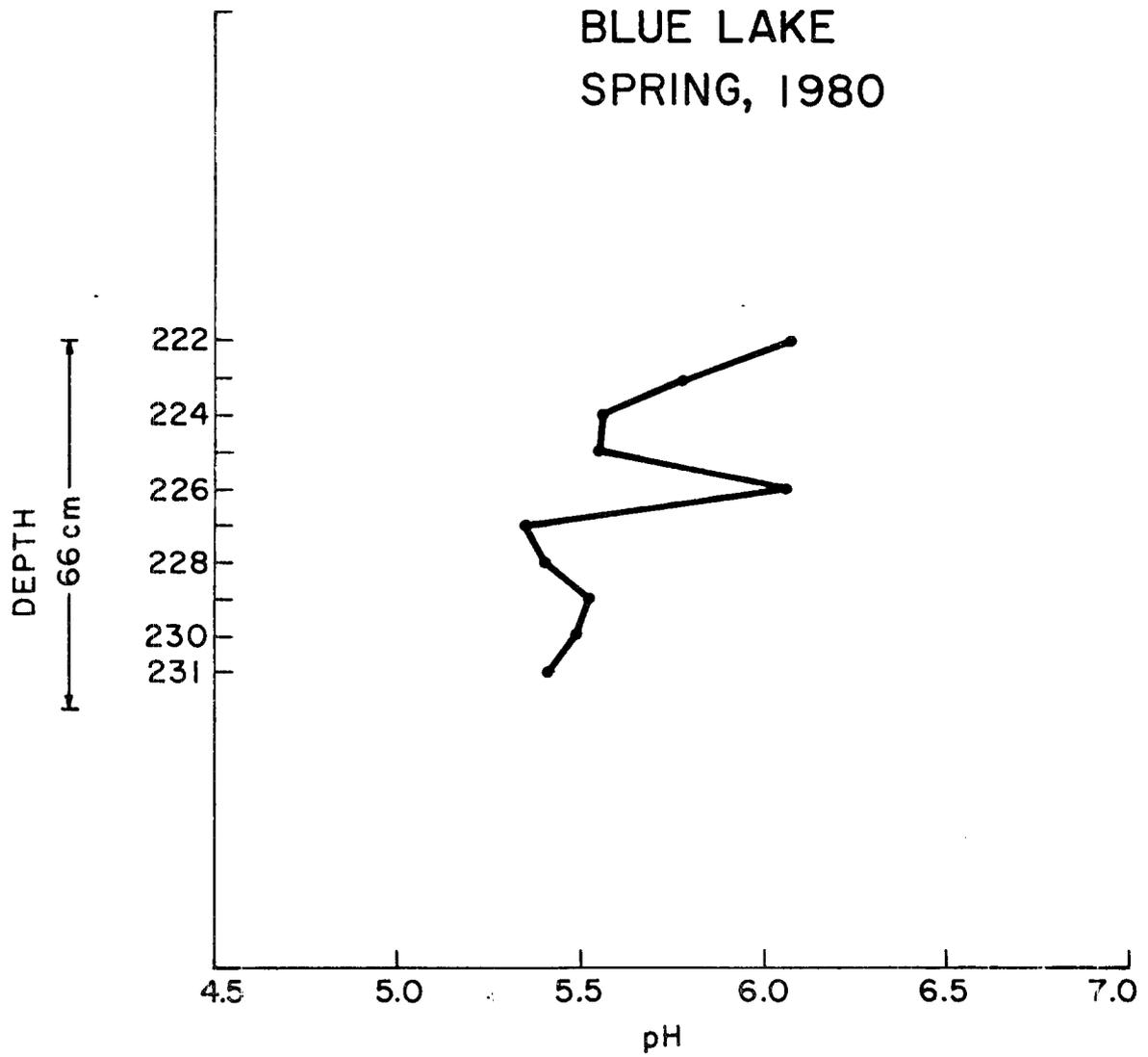


Figure 3.14a. Profile of pH within the snowpack for Blue Lake, spring 1980. Details the same as Figure 3.1a.

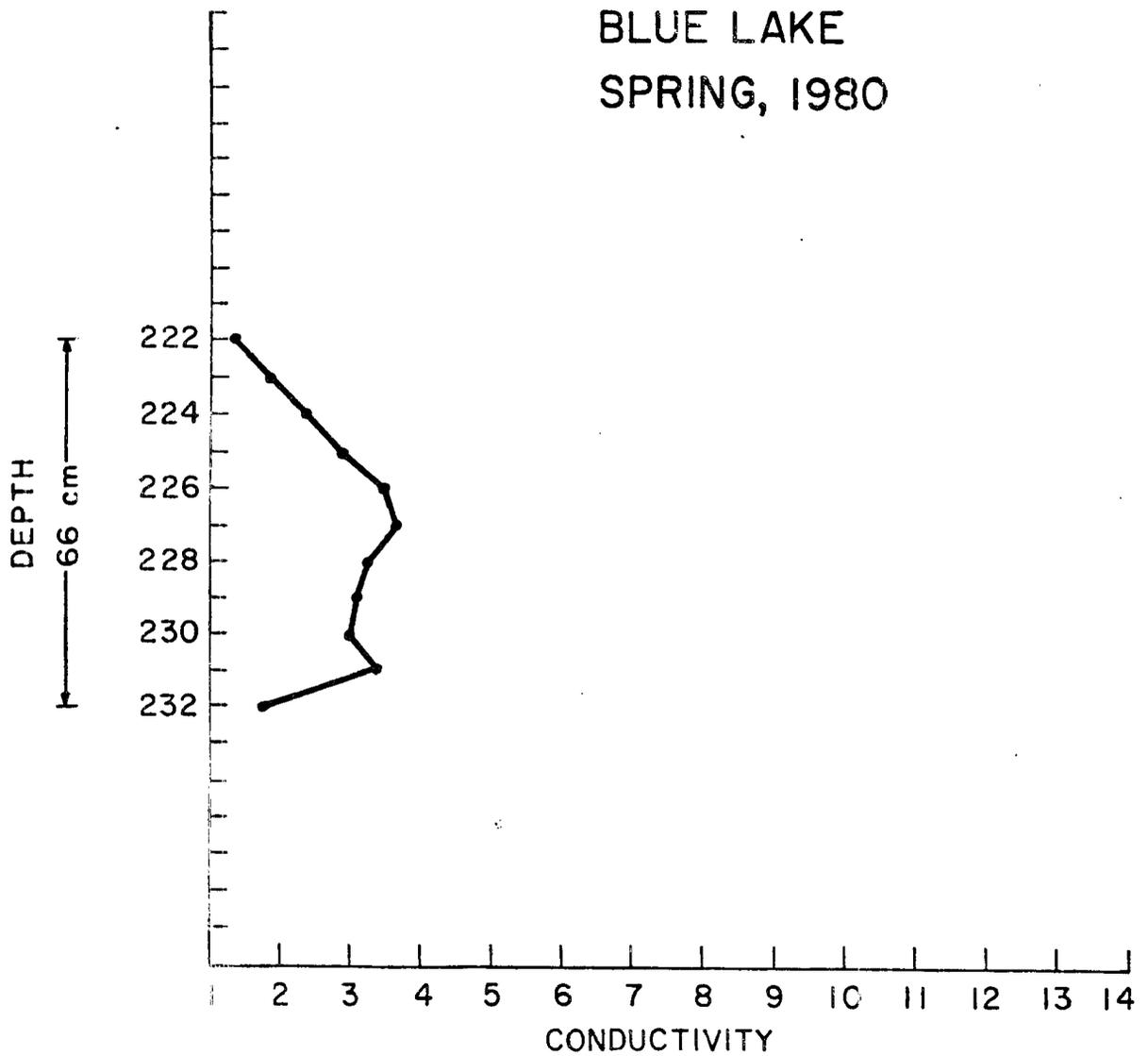


Figure 3.14b. Profile of specific conductivity within the snowpack at Blue Lake, spring 1980. Details the same as Figure 3.1b.

fairly uniform pH values in the lower two fifths of the snowpack, a feature similar to the snowpit at Milner taken in March. The difference between Milner and Blue Lake is that the upper layers of the Milner snowpit were fresh snow, with an acidic component deposited on acidic snow which had undergone periods of melt during the daytime. This allowed some percolation of liquid water to adjacent layers in the snowpack, spreading hydrogen ions uniformly. The Blue Lake site is all aged snow, so this process had already occurred and the hydrogen ions had already been removed into the runoff, leaving a relatively neutral profile.

The Blue Lake snowpit profile taken during this sampling period, exhibited an interesting feature. When compared with the Blue Lake profile from the previous sampling period, a spike remains in the pH which is on the alkaline side of equilibrium with atmospheric CO_2 , while all low pH values are absent. It is suggested that this feature may be due to aerosols originating in alkaline soils and that these aerosols are not as water soluble as the acidic components in the snowpack. Therefore, they remain in the snowpack well past the initial runoff, and are not available in the initial runoff to neutralize the acidic components. The high surface pH value in the Blue Lake profile is probably due to dry deposition of dust during the springtime fair weather.

An interesting aside to the May data are the topmost samples from Rabbit Ears Pass and Blue Lake (sample numbers 204 and 232 from Figures 3.13a and 3.14a). These samples contained volcanic ash from the May 18 eruption of Mt. St. Helens. It was thought that since volcanic eruptions are often quite high in sulfur compounds and hence, often quite acidic (Hammer, 1980), that the ash from this eruption could affect the

acidity of the snowpack in Colorado. As it turns out this particular volcanic eruption was very low in sulfur content, which is reflected in the almost neutral pH values obtained, 5.45 at Rabbit Ears Pass and 5.70 at Blue Lake.

3.3 1981 Sampling Period

The samples from this sampling period at Wolf Creek Pass and Rabbit Ears Pass are the only ones which can be used for interannual comparison since the remainder all underwent significant melt within the snowpack. The pH and conductivity profiles from Wolf Creek Pass and Rabbit Ears Pass are shown in Figures 3.15a & b and in 3.16 a & b.

The effect of acid precipitation is evident at both of these sites once again. The median values at both sites are similar to the previous year's median, in this case being 5.19 at Wolf Creek Pass and 5.09 at Rabbit Ears Pass. The number of pH values less than 5.0 is reduced, there being only five as compared with nine of the 21 samples at Wolf Creek Pass and only three out of 17 samples at Rabbit Ears Pass. Wolf Creek's lowest pH value was 4.71 and Rabbit Ears' lowest was only 4.92.

The remaining sample values from the other sites are of little significance due to the melt which had taken place in the snowpack. The pH and conductivity values from these sites are found in Appendix A.

The snowpack depth at Rabbit Ears Pass and Wolf Creek Pass was about two thirds as deep as the year before. In general the acidic characteristics of the snowpack were similar to the snowpack characteristics from the previous year. As well, the effects of orography on precipitation at these sites will be the same. There is a tendency for the data from 1981 to be slightly less acidic in terms of the median value and the low pH values. This can be attributed to the warmer tem-

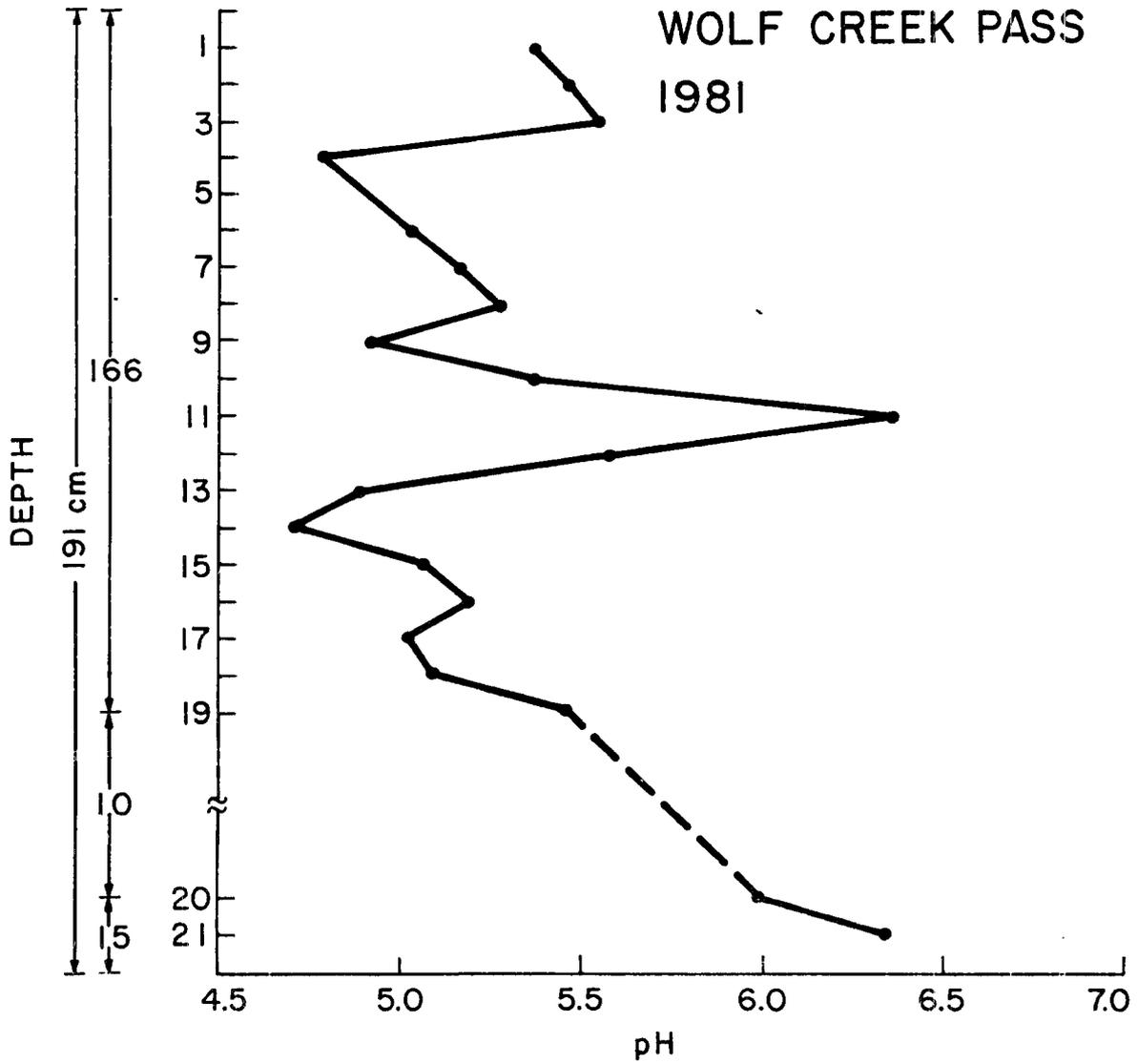


Figure 3.15a. Profile of pH within the snowpack for Wolf Creek Pass, 1981. Details the same as Figure 3.1a.

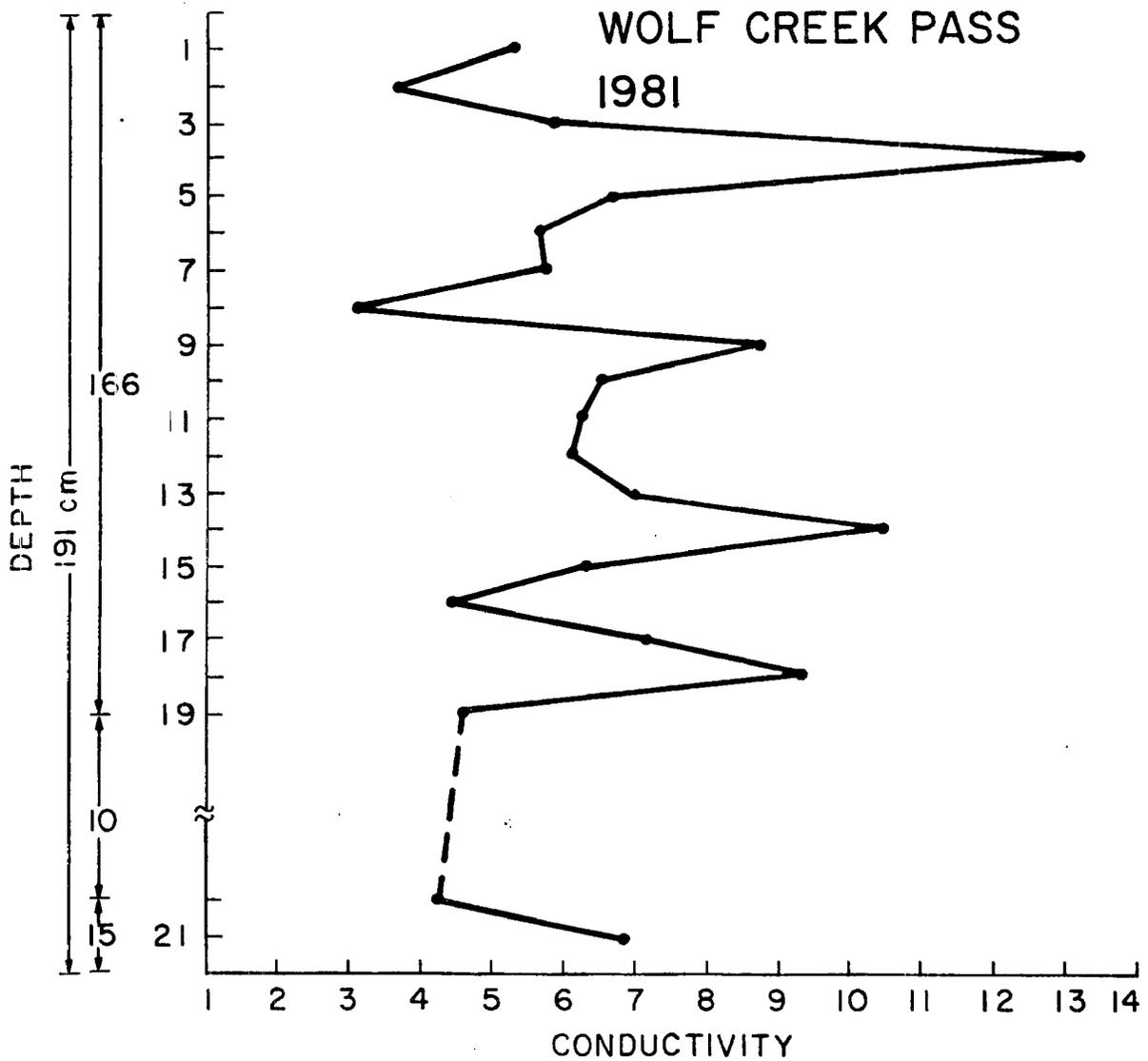


Figure 3.15b. Profile of specific conductivity within the snowpack at Wolf Creek Pass, 1981. Details the same as Figure 3.1b.

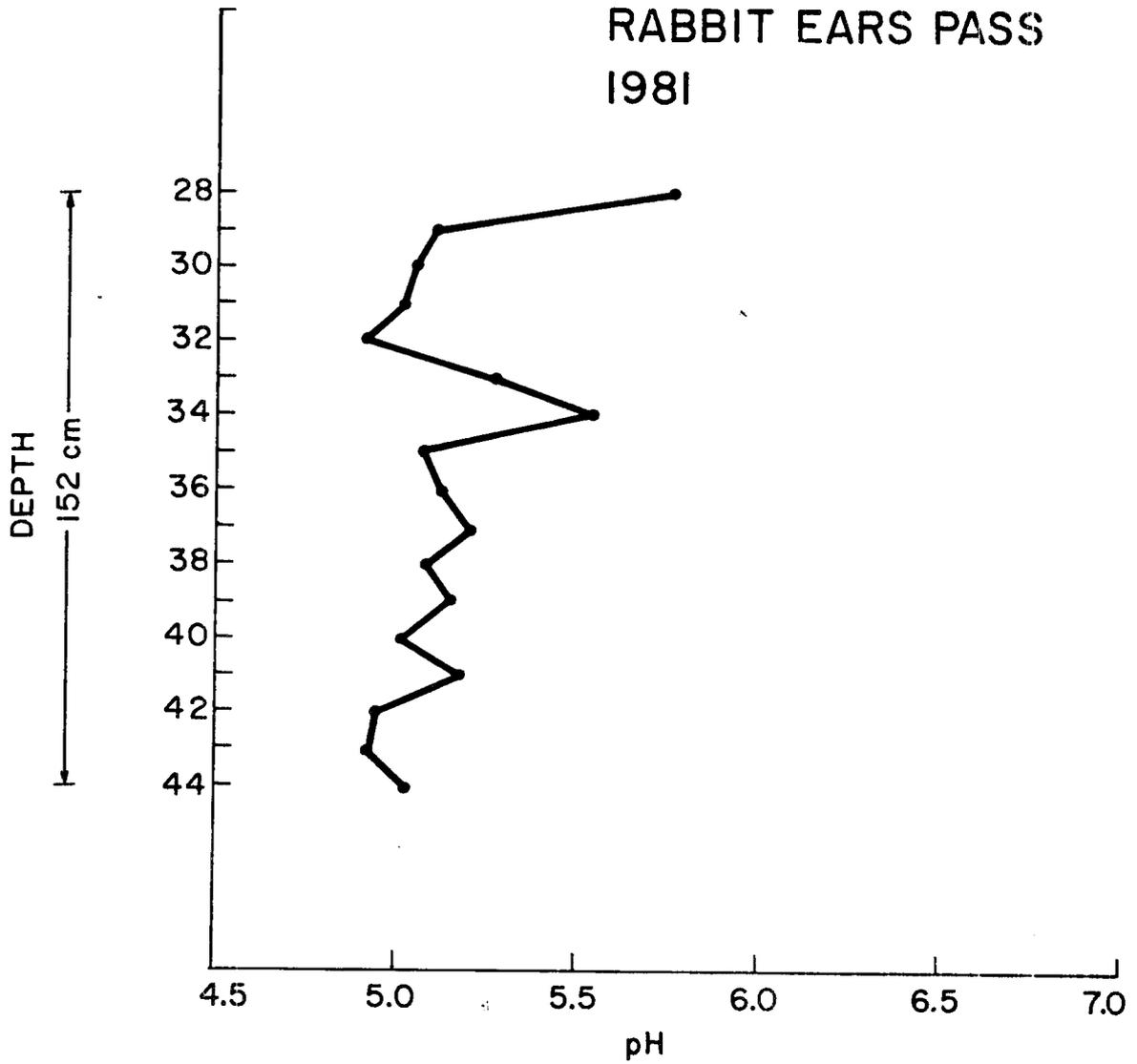


Figure 3.16a. Profile of pH within the snowpack for Rabbit Ears Pass, 1981. Details the same as Figure 3.1a.

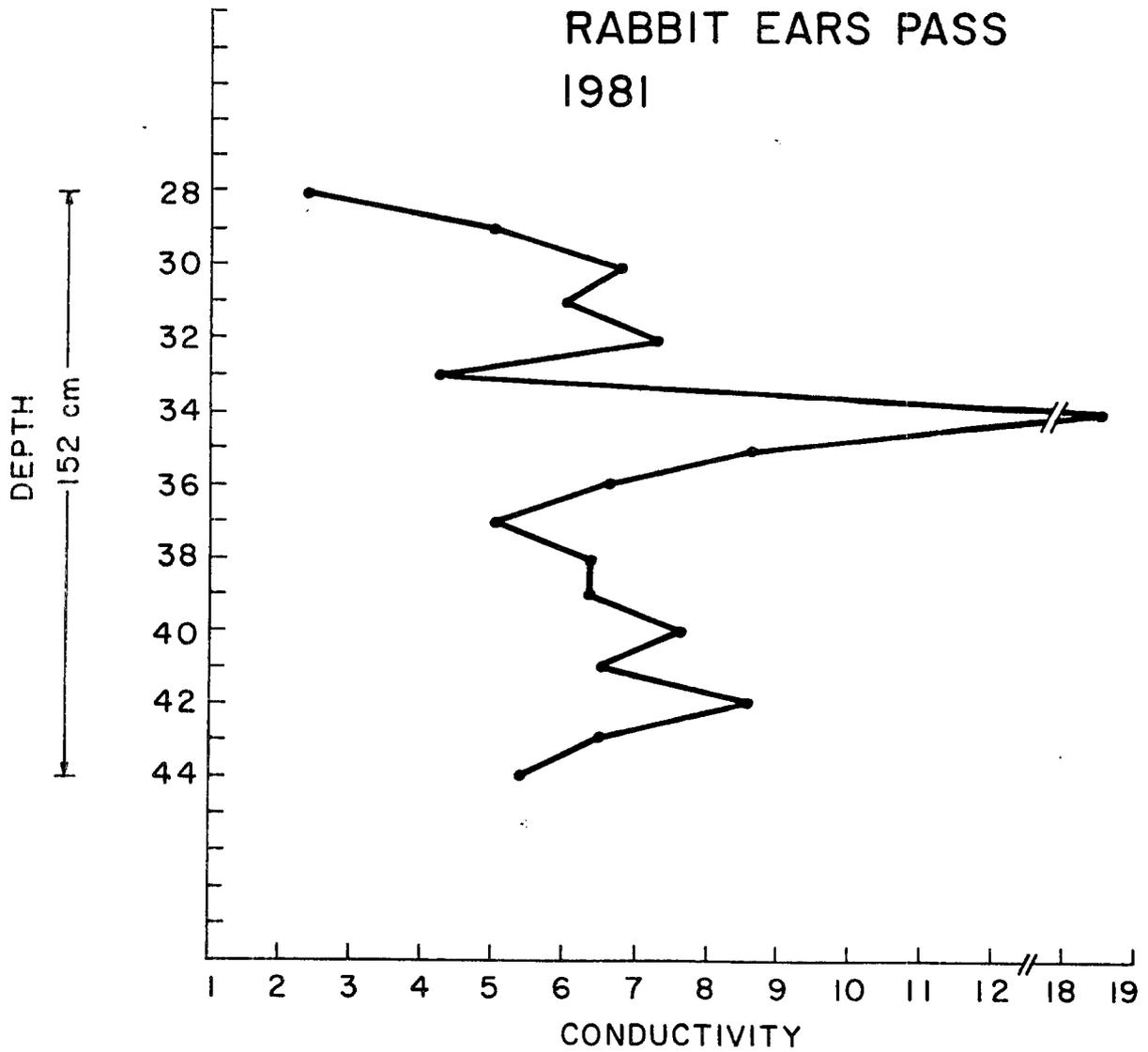


Figure 3.16b. Profile of specific conductivity within the snowpack at Rabbit Ears Pass, 1981. Details the same as Figure 3.1b.

peratures and the greater time between storm episodes of the season allowing a degree of melt to take place, increasing some of the lower pH values. Secondly, there was less total snowcover upwind of the sites during this drought year, allowing more dust from the generally alkaline soils upwind of the region to be more easily incorporated in the precipitation or settle on the snowpack, thereby increasing the pH.

The feature that was different about the Wolf Creek and Rabbit Ears sites at the time of this sampling, was that melt had started to occur in the upper layers, evidenced by the snowpack structure. This provided an opportunity to investigate the leaching of ions through the snow just after melt initiated. The topmost layers at Wolf Creek Pass were samples 301, 302, and 303 in Figure 3.15a. These pH values were around 5.4. Sample 304, taken in the unmelted below sample 303, drops to a pH of 4.8. As well as this, the specific conductivity jumps from 5.9 micromhos cm^{-1} to 13.2 micromhos cm^{-1} . The pH then rises steadily in the next several samples, but still is fairly acidic. A similar situation occurs at Rabbit Ears Pass (Figure 3.16a). Here the upper layers were not quite as melted, so they retain more of their acidic content. There is once again a minimum in pH just below the melted upper layers.

CHAPTER 4 DISCUSSION AND CONCLUSIONS

From the results presented in the previous chapter, several important features should be noted. The most important feature of this study is the baseline of pH and conductivity data provided from around the state of Colorado. This is the first study of the pH and conductivity of the snowpack to take place in Colorado.

The lack of a full ion analysis and the inability to resolve discrete snowfall events make definitive statements about the sources of acidic pollutants at the various sites difficult. The variations in the pH values between sites are, however, suggestive. The relative importance of long range transport of acidic components versus the importance of local sources of acids is discussed. This study has also suggested that alkaline components may play a role in the amount of acidity found in the Colorado mountain snowpack. Some ideas on the reasons for the variability of the pH within the snowpack at some sites and other possible explanations for the overall variability will also be considered.

Some supplementary observations and conclusions can also be made from the results of this study. These include (1) ion migration within the Colorado snowpack due to melt, (2) the effects of the 18 May 1980 eruption of Mt. St. Helens, (3) the relationship of pH to conductivity in the Colorado snowpack, (4) the utility of the sampling and analysis technique, (5) the effect snow grain type has on the pH, and (6) finally a comparison of the data values obtained in this study with those obtained from other parts of the world. These various observations and conclusions will be discussed in this chapter.

4.1 Baseline Information

The feature of this study which is of the greatest value is the baseline of information provided on the pH and conductivity of the winter precipitation in varying regions of the state. This baseline covers areas on the western slope, the central mountains, and the eastern slope of the Colorado Rockies. Some of the sites in these areas are potentially affected by local acidic pollutant sources while others will only be affected by longer range transport. Before the effects of long range transport versus local contributions to acids in the snowpack are examined some general comments on the indications from this baseline are in order.

The results of this study indicate that at the present time acids in the snowpack do not pose a significant threat to the region. None of the pH values in this study were extremely low. In order for acid snow to pose a significant threat to the environment, aquatic ecosystems being the most susceptible to acid snow's effects, the mean pH value of the entire snowpack must be below even the lowest values found in the Colorado snowpack.

Even though at the present time there appears to be no significant threat to Colorado from acid precipitation, a change could take place. Energy development is taking place along the western slope of the Colorado Rockies and the population is expanding along the Front Range. With this development and expansion, further release of acidic contaminants will take place, potentially leading to more areas being affected by acid precipitation and increased effects being felt in areas where acid precipitation is already occurring.

Because of the potential for an increase in acid precipitation in the state, a good baseline of information is crucial to attempts to monitor such a spread in the future. The variety of locations used for sites over the span of the winter season, provided through sampling of the winter snowpack, has provided such a baseline. This baseline can be used for comparison with future studies, as an indication where impacts from future energy development might occur, and to indicate where further study should take place.

4.2 Local Sources Versus Long Range Transport

The quantities of acid in the Colorado snowpack are not great at any individual site. However, there are differences in the amounts of acid found around the state. These differences appear to be tied to the presence or absence of local sources of acidic pollutants in conjunction with orographic precipitation enhancement.

Effects of Local Sources

The sites where the snowpack exhibited the most acidic pH profiles were linked to the presence of a local source of acidic pollutants in conjunction with air flow from a direction which would enhance orographic precipitation when acidic contaminants from the local source are advected over the area. Enhanced washout of acidic contaminants should occur with enhanced precipitation, such as that induced by orography. Results from an orographic precipitation model (Rhea, 1978) were used to indicate which wind directions would most greatly enhance the precipitation at the various sites. It was found that situations which would advect acidic contaminants to a site were also situations which would maximize the orographic component of precipitation. In the case of Wolf Creek Pass, Rabbit Ears Pass, Blue Lake and Milner, the source of acids

appears to be coal-fired power plants in the region. In the case of Long Lake, the source appears to be the Front Range Urban Corridor.

Some sites, such as Red Mountain Pass, even though in close proximity to a contaminated area, such as Wolf Creek Pass, exhibited a fairly low amount of acid in the snowpack. The differing factor was the amount of precipitation enhancement from orography. A situation which would potentially bring acidic contaminants to both of these sites is southwesterly flow. Under this flow condition, Wolf Creek Pass is under a maximum in orographic precipitation influence, while Red Mountain Pass is at a minimum due to shadowing from upwind barriers. Red Mountain Pass realizes increased orographic enhancement with northwesterly flow such that the impinging air passes over relatively unpolluted areas.

It must be noted that air flow in mountainous terrain is usually extremely complicated. The relationship between the local sources and the orography is a large scale feature forcing the enhancement of acids in the precipitation. An individual precipitation event can be greatly affected by mesoscale flow features which may dominate a particular situation. Detailed analysis of the mesoscale meteorology and real time observations of the precipitation chemistry are necessary to resolve these types of features; this is beyond the scope of a snowpack sampling study of the kind described here. The present study strongly implicates local sources as the primary contributor to the low pH values found in the winter precipitation of Colorado's mountain regions.

Effects of Long Range Transport

Widespread acidification of precipitation, as hypothesized by Lewis and Grant (1980), would imply transport of acidic pollutants over long distances, as in the case of Scandinavia or the northeastern United

States, and generally acidic values where ever precipitation samples are taken. The study of Lewis and Grant (1980) was carried out on the eastern slope of the Colorado Rockies. If long range transport from the west would affect this site, it might be expected that acidic precipitation would be found to the west of their study area. This situation does not occur. Only certain sites in the present study showed acidic pH profiles; these were near identifiable local sources of acidic pollutants. The site at McClure pass, on the western edge of the Colorado Rockies showed fairly high pH values. The samples from this site occasionally showed some increase in acidity in its pH profile, indicating that acidic sources from a farther distance away can potentially affect the area; the sporadic nature of these acidic intrusions precludes any widespread effects from long range sources. The sites at Climax and Guanella Pass showed no pH values which were very acidic, and they receive most of their precipitation from flow with a westerly component. This indicates that even the sporadic intrusions of acidic contaminants which are seen on the western edge of the range, are removed by the time the air reaches the central Rockies, much less the eastern slope where the study of Lewis and Grant (1980) took place. It should be remembered that during long range transport from the west to Colorado, acidic material must pass over the Great Basin. In this process these acidic materials may tend to be neutralized by the alkaline dust which is produced from the soils of this region. This study suggests that at the present time, long range transport from the west is not a dominant contributor to the low pH values found in the winter precipitation found in the Colorado Rockies, nor is it likely to become so in the near future.

4.3 Alkaline Components

The role alkaline components may play in the total acidity of the Colorado snowpack should not be overlooked. Approximately 19% of the samples taken during the first sampling period had pH values in excess of 5.6, and most of these came from sites on the western slope or the central mountains. This suggests that alkaline dust potentially advecting in from the Great Basin may affect the level of acidity being found in the Colorado snowpack.

The samples from McClure pass and Red Mountain Pass showed the greatest effect from alkaline components. One third of the samples taken from each of these sites had pH values in excess of 5.6. Wolf Creek Pass had the highest pH value obtained in the study. The first two sites were "clean" sites, while the latter site was considered "contaminated." The presence of these higher pH values indicate that during conditions where local sources of acidic components were not likely to dominate the pH of the snow, alkaline components were able to dominate, yielding pH values in excess of 5.6. This occasional dominance of the pH by alkaline components also suggests that the lower pH values may be offset somewhat by these components. In the absence of the alkaline component source provided by the Great Basin, the Colorado snowpack might exhibit much lower pH values.

Although the results of this study have so far suggested that local sources of acidic pollutants are the dominant feature responsible for the pH values found in the Colorado snowpack, it is also possible that long range transport of acids does occur with greater frequency than indicated here. A dominance of alkaline components would mask this effect of long range transport. Even if this is the case, the potential

environmental hazard posed by an acidic snowpack is reduced by the presence of alkaline components. A full ion analysis of the samples would be necessary to resolve this question.

4.4 The Variability of pH within the Snowpack

When one examines the pH profiles of the snowpack from Rabbit Ears Pass and Wolf Creek Pass, some similarities and differences are apparent. At both sites about one half of the pH values fall below 5.0. The variability in pH values at Wolf Creek Pass is much greater; some of the values are well above a pH of 6.0. At Rabbit Ears Pass no pH values are even above 5.6. This effect can be explained in terms of proximity to a power plant and the channelling effects of local topography.

The Four Corners Power Plant is 150 km. away from Wolf Creek Pass and there is no local topography which would preferentially channel effluents from this source to Wolf Creek Pass. Only relatively specific wind directions will cause the power plant to affect Wolf Creek. Also, the desert areas of northern Arizona and southern Utah are to the west of this site. These areas are sparsely vegetated and have alkaline soils. Westerly winds can potentially advect high quantities of alkaline dust to Wolf Creek Pass and at the same time carry the effluents from the power plant away from the site, thus causing high pH values in the snowpack.

Rabbit Ears Pass is located only 46 and 68 km. east from the Hayden and Craig Power Plants in the Yampa River Valley. Rabbit Ears Pass receives most of its precipitation from either northwesterly or westerly flow events. Precipitation from the southwest is shadowed by the Flat Top Mountains. Under the heavier precipitation conditions, air and the effluent from the power plants is channelled up the Yampa Valley to the

barrier on which Rabbit Ears Pass lies. Also, the land to the west of Rabbit Ears Pass is rangeland with more vegetation than the desert areas to the south, reducing the transport of alkaline dust to the site. The absence of the alkaline dust source and the channelling effects of the local topography cause the Rabbit Ears Pass site to have more uniformly low pH values.

4.5 Other Possible Explanations

Other possible explanations for the variation in pH observed between sites includes cloud physics differences and a variation in the amount of alkaline ions in the precipitation. Both of these will be addressed here, but both seem to be weak possibilities compared with the effects of local sources in conjunction with orographic precipitation enhancement mentioned earlier.

It might be argued that cloud physics differences and the accompanying differences in the mechanism by which acid may become incorporated in snow may be the reason for the observed variability observed between different sites. Both Rabbit Ears Pass and Wolf Creek Pass had more low pH values. The snowfall at these sites is also more heavily influenced by riming processes, hence, liquid water plays a greater role in the precipitation process at these sites. As mentioned in Chapter 1, the presence of liquid water may be the dominating factor in the acid snow formation process. Therefore, it may be argued that the presence of riming is the reason for the low pH values at these sites. This well may be a part of it, but when one looks at Blue Lake, many low pH values were also observed. The snowfall process at Blue Lake and Long Lake is dominated by diffusional ice crystal growth. If only the cloud physics differences were responsible for the observed differences in pH between

sites, Long Lake and Blue Lake should not exhibit the pH profiles that they do.

Variability in the amount of alkaline ions is a possible explanation for the variability of pH between sites, but not a likely one. If the variability in alkaline ions is responsible, one would expect that all sites would have similar pH profiles, since alkaline sources are large and fairly widespread. The one factor which is different between sites with more acidic pH profiles and those without is the presence of a local source of acidic pollutants in conjunction with orographic precipitation enhancement.

4.6 Ion Migration Within the Snowpack

The effects of ion migration within the snowpack due to the percolation of meltwater were evident in this study. The samples taken from Rabbit Ears Pass and Blue Lake in the spring of 1980 showed approximately one half of the hydrogen ion concentration in the snowpack as the same sites showed earlier in the year before any melt took place. This is consistent with other studies of ion washout in the snowpack (Oden and Bergholm, 1973; Johanessen and Henriksen, 1978). Besides the total washout of ions observed, a migration of ions was noted in the results from the samples collected at Wolf Creek Pass and Rabbit Ears Pass in 1981. Below the top layers of the snowpack, at each of these sites, where some melt had started, the pH values were significantly reduced and the conductivity values were significantly increased, indicating that the ions within this layer had been flushed out and were then carried to the next lower, unmelted layer. It would be expected that this process would continue as the snowpack melted so that the initial runoff

would be enriched in ions as compared with the snow which originally fell.

4.7 Effects of the Mt. St. Helens Eruption

As described in the previous chapter, some of the samples from the May 1980 sampling period contained fresh deposits of ash from the 18 May 1980 eruption of Mt. St. Helens. These deposits did not significantly affect the pH or the conductivity of the snowpack samples.

4.8 Relationship Between pH and Conductivity

If hydrogen ions were the dominant contributor to the total conductivity, it would be expected that a strong correlation would be found between the pH or hydrogen ion concentration and the conductivity. This was not the case. When the pH values of the entire data set were linearly regressed against the conductivity, a correlation coefficient of only 0.355 was found, indicating that only 12.6% of the variation in the conductivity was explained by the pH. When the same was done with the hydrogen ion concentration as calculated from the pH, the relationship was even weaker. This regression yielded a correlation coefficient of 0.082, which means that the hydrogen ion concentration only explained 0.7% of the variation of the conductivity. Similar results were obtained when the same comparisons were made on the data taken from each site individually. This indicates that hydrogen ions are not the dominant contributor to the conductivity of the overall data set. The more acidic samples, which have more hydrogen ions, usually exhibited higher conductivities since hydrogen ions are quite mobile.

4.9 Sampling and Analysis Technique

The sampling technique used in this study was satisfactory. The equipment necessary for its implementation was inexpensive and fairly

easily obtainable; namely a shovel, Zip-lock bags and polyethylene containers. Digging of a snowpit allowed easy identification of layers within the snowpack. The greatest disadvantage of the technique is the time involved in obtaining the samples and the inability to obtain a uniform horizontal cross section of each individual sample. Both of these deficiencies can be remedied by using snow coring tubes made out of inert materials, so the sample will not be contaminated by the sampling device. Using a snow core, one can easily obtain several profiles in the same vicinity, insuring the representativeness of the sample. Also, a tube will provide a uniform horizontal cross section. This will allow one to weight the chemical value of each sample by the water equivalent or mass of the sample, thereby giving a more accurate representation of the ionic content of the entire snow profile.

The analysis technique used was satisfactory as well. Other pH measurement techniques occasionally used in conjunction with the meter would be useful as a check of the meter's accuracy. The most desirable addition to this study would have been a complete ion analysis, to determine the contributing anionic components to the measured pH values. All samples would not have to have the full analysis performed on them. The pH values would be used to determine which samples would be of interest in a full analysis.

4.10 Variations of pH with Snow Type

In the study of Clement and Vaudour (1967), note was taken of variations in pH with respect to snow type. There it was found that less dense, powdery or fresh snows exhibited generally lower pH values. The spread of these values was, however, high. It was determined that a similar comparison with the present data set would be of interest.

At some of the sites, as noted in Chapter 2, the upper layers of the snowpack were composed of fresh, powdery snow. Of the 14 powdery samples obtained, only 4 had pH values greater than 5.2. Eight of the 14 samples had pH values less than 5.0. At Climax, where the topmost sample was only fresh snow in which the dendritic crystals could be easily distinguished, the topmost sample yielded a pH value of 6.75. It should be remembered that the Climax site had the least acidic pH profile of any of the sites. Lower pH values are generally found in the fresher, less dense snow samples, consistent with Clement and Vaudour (1967). Clement and Vaudour (1967) attributed the reduced pH found in the samples near the snowpack surface to excess CO_2 being incorporated into the sample from the air trapped between crystals of less dense snow. This does not seem likely since the samples in the present study, which showed similar results, were not analyzed immediately. This allowed the air spaces between crystals to fill. Another hypothesis would be that these powdery layers, being fairly fresh, have not yet interacted with any dust which might fall out onto the snow, potentially providing a neutralizing effect.

Another notable feature of the snowpack at some of the sampling sites was the presence of depth hoar. Depth hoar is a manifestation of vapor diffusion within the snowpack along a temperature gradient. The absence of any agreement between this phenomenon and the pH of the sample seem to indicate that there is no preferential migration of acidic ions within the snowpack due to vapor diffusion.

Samples collected at or below an ice lens usually exhibited low pH values. This, as mentioned earlier, is due to the migration of ions in

the meltwater. Ice lenses are manifestations of small amounts of melt at the surface which are later covered by a fresh layer of snow.

4.11 Comparison With Other Data

In order to put the pH values obtained from this study into perspective, a comparison with other pH values obtained from snow from other parts of the world has been made. To facilitate this process, a summary of other work from around the world is shown in Table 4.1. The results are listed according to the reference and include the area from which the sample was obtained and pertinent comments, as well as a summary of the pH values.

From Table 4.1, it is evident that the pH values obtained in the present study are similar to those found in other, relatively uncontaminated areas of the world. Examples being the southern French Alps, background levels from Greenland ice cores, and northern Africa. There seems to be no indication from this study that the acid precipitation phenomenon is anywhere near as great as in Scandinavia or the Adirondack Mountains of New York. In these places the mean value of the snowpack pH was often around 4.5, a mean value falling even lower than any of the individual samples collected in the present study.

As well as the data presented in Table 4.1, some mention should be made of the pH values obtained from the Colorado collection sites of the National Atmospheric Deposition Program during the winter of 1979-80. The pH values ranged from 4.23 to 6.22. None of the sites reporting were located in the high mountain regions of the state. The pH values are from samples collected at weekly intervals.

TABLE 4.1

pH Values From Other Areas

<u>Reference</u>	<u>Location</u>	<u>pH Values</u>
Vimont (1980-1981)	Colorado	4.63 - 6.92
Barrett and Brodin (1955)	Sweden	4.7 - 4.8 Mean Feb. - March Values
Brimblecombe (1980)	Northern Africa	5.2 - 6.7
Clement and Vaudour (1967)	Southern French Alps	4.4 - 7.0 Most Around 5.4
Elgmork et al. (1973)	South Norway Snowpack Profiles	3.4 - 5.1
Feth et al. (1964)	Western U. S.	4.2 - 7.7
Forland and Gjessing (1975)	Norway	5.0 - 6.5
Galvin and Cline (1978)	Adirondacks	4.2 - 4.3
Hagen and Langeland (1973)	South Norway Snowpack Profiles	3.7 - 4.8
Hammer (1980)	Greenland Ice Cores	5.52 - 5.70 Background 4.64 - 5.30 After Volcanic Eruptions
Herman and Gorham (1957)	Nova Scotia	5.6
Hultberg (1977)	Sweden Snowpack Profiles	4.4 - 4.5
Johanessen and Henriksen (1978)	Norway	3.98 - 4.91
Likens et al. (1979)	Greenland Ice Sheets	Greater Than 5.0
Thorn and Hall (1980)	North Sweden and Colorado	4.5 - 5.5
Wright and Dovland (1978)	Norway Snowpack	Less Than 4.7 Over Large Area

CHAPTER 5 SUMMARY

The phenomenon of acid precipitation has gained increasing interest over the last 30 years. The geographical regions which have been focused on are the Scandinavian countries and the northeastern United States, since these regions are downwind from industrialized regions which release acidic contaminants and have suffered environmentally from acid precipitation's effects. Only recently have acid precipitation studies focused on the western United States. Studies in the Colorado Rocky Mountains indicated that acid precipitation does exist there. These studies did not, however, indicate the areal extent of the phenomenon. Further study was necessary to determine this, hence, the present study was undertaken.

The present study examines the pH and specific conductivity values of snowpack samples taken from around the state of Colorado. Snowpack sampling is a useful tool for several reasons. 1) The majority of the precipitation at higher elevations in Colorado falls as snow during the winter months, building the winter snowpack, which then remains until the spring thaw. 2) The snowpack has the advantage of being the accumulated total of the winter season's precipitation, which preserves ionic constituents, including acids, until the first runoff takes place. Because of this property, a site can be sampled at a single time and a profile of the entire season's precipitation can be obtained. Sampling sites were chosen throughout the mountain regions of the state such that some would potentially be affected by local sources of acidic pollutants, such as coal-fired power plants or the Front Range Urban Corridor, and others would likely be free from such effects and represent the amount of acid entering the state from the west. Sampling was accom-

plished by digging a snowpit at the various sites and pressing clean polyethylene containers into the cleaned snowpit wall. The samples were taken back to the laboratory in a frozen state. They were then melted and analyzed.

The results of the study showed that none of the pH values were extreme. The range of pH values examined in the study was 4.63 to 6.92. Approximately 20% of the samples were below a pH of 5.0, 60% between 5.0 and 5.6, and 20% above a pH of 5.6. Individual sites varied. Half of the samples from sites near local sources of acidic pollutants had pH values less than 5.2 and at two of these sites half of the pH values were less than 5.1. The sites removed from local sources of acidic pollutants had only a few samples which fell below a pH of 5.0. The results also indicated that orographic precipitation enhancement affects the amount of acidic contaminants found at a particular site. Two sites which would have potentially been affected by the same local source exhibited markedly different pH profiles. The site with the low pH values was at a location which realized a maximum in orographic precipitation enhancement in the areas downwind of acidic pollutant sources. The site with fewer low pH values is in an area with a minimum in orographic enhancement when winds are from the direction of the pollutant source.

From these results, a number of conclusions and observations can be made. The most significant feature of the study is the baseline of pH and conductivity information established on the wintertime precipitation in the Colorado Rockies. This information has covered a broad area of the state and a variety of conditions. It has shown that none of the pH values were extremely low or extremely high. With the accelerated

amount of energy development and population expansion taking place in the region, acid precipitation may increase. This study will be useful as a comparison for studies trying to detect any change in the effect or amount of acid precipitation in the region.

Because of the presence of local sources of acidic pollution near some of the sites and the absence of local effects at other sites, the relative importance of local effects versus long range transport to the measured pH values can be inferred. Samples from sites near local sources of acid pollutants that receive a maximum in orographic precipitation enhancement when directly downwind from the source, exhibited the most consistently low pH values. Samples from sites free from local effects, "clean" sites, showed higher pH values. These "clean" sites on the western edge of the state had a few low pH values, suggesting that sporadic intrusions of acidic contaminants come into the state. "Clean" sites in the central mountains had relatively high pH values overall, indicating that acidic contaminants are washed out by the time the precipitating air mass reaches the site. Therefore, local sources seem to dominate the low pH values at individual sites.

The "clean" sites on the western edge of the state also have more pH values above 5.6, suggesting that alkaline components, potentially from the alkaline soils of the Great Basin, may play a significant role in the total acidity measured. Therefore, acidic contaminants may be transported over long ranges, but not be detected because they are being neutralized by alkaline components. In the absence of the alkaline soils of the Great Basin, the total acidity measured might be much greater in the region.

In addition to these major points, some secondary observations and conclusions were also made. These include ion migration with the initial meltwater within the snowpack, the absence of effect on the pH or conductivity from the ash fallout of the Mt. St. Helens eruption, the lack of correlation between pH and conductivity, the utility of the sampling and analysis technique, the variations of pH with snow type, and comparison with other snow and pH measurements in other parts of the world.

5.1 Suggestions for Further Research

A continuation of snowpack sampling, as described in this study, would be useful. From such a continuation, the network could be expanded and temporal trends might be established. If a continuation takes place, more detailed ion analysis would be critical. The elements and compounds found in the snowpack can be used to more accurately trace sources and may well affect cloud processes. A detailed ion analysis would also help in determining the role of alkaline dust in neutralizing acids found in the snowpack.

Detailed mesoscale analysis, for areas of interest, is also suggested. Sampling and analyzing individual snowfalls during their occurrence, in conjunction with mesoscale meteorological data, will yield a better understanding of acid transport in an area and indicate which acidic components dominate. This type of research would best be carried out first in areas where acid precipitation already exists to gain insight about the processes. Then it should be extended to areas where development is taking place.

Further understanding is also needed of the process by which acids become incorporated into Colorado's winter precipitation. Chemical

analysis of cloud water versus ice should be made in order to better determine the role of riming on the acids found in snow. A better understanding of the cloud processes related to acid precipitation is the most difficult to gain, but also the most important.

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APPENDIX A

Miscellaneous Data Mentioned in Text

Red Mountain Pass Second Snowpit

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
114	6.12	6.26	0.54
115	3.67	5.53	2.95
116	5.14	5.07	8.51
117	9.41	4.83	14.79
118	6.98	6.51	0.31
119	5.38	5.43	3.72
120	3.92	5.17	6.76
121	4.27	5.16	6.92
122	4.09	5.17	6.76
123	3.20	5.40	3.98
124	5.27	5.10	7.94
125	2.56	5.46	3.47
126	9.74	6.97	0.11
127	75.61	7.61	0.02
128	60.24	7.82	0.02
Mean	13.71	5.35	4.45
Median	5.27	5.43	3.72

Silverton Surface Samples

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
129	7.43	6.13	0.74
130	6.92	6.48	0.33
131	5.00	5.60	2.51
Mean	6.45	5.92	1.19
Median	6.92	6.13	0.74

Winter Park, Spring 1980

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
192	2.13	5.62	2.40
193	2.41	5.70	2.00
194	2.25	5.60	2.51
195	3.31	5.76	1.74
196	3.80	5.24	5.75
197	3.14	5.56	2.75
198	3.41	5.39	4.07
199	6.47	5.40	3.98
Mean	3.37	5.50	3.15
Median	3.14	5.56	2.55

Cameron Pass

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
200	4.05	5.33	4.68
201	8.99	5.00	10.00
202	4.76	5.16	6.92
203	3.86	5.33	4.68
Mean	5.41	5.18	6.57
Median	4.05	5.16	4.68

Steamboat Springs Snowfall

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
233	10.95	4.68	20.89

Blue Lake, 1981

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
322	2.98	5.35	4.47
323	3.52	5.30	5.01
324	4.12	5.25	5.62
325	4.34	5.17	6.76
326	4.55	5.28	5.25
327	3.85	5.42	3.80
Mean	3.89	5.29	5.15
Median	3.85	5.28	5.01

Rabbit Ears Pass, Repeat of Top Samples, 1981

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
345	2.26	5.77	1.70
346	4.35	5.25	5.62
347	5.31	5.08	8.32
348	8.62	4.95	11.22
Mean	5.14	5.17	6.71
Median	4.35	5.08	5.62

McClure Pass, 1981

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
349	3.72	5.90	1.26
350	8.46	6.55	0.28
351	2.43	5.73	1.86
352	4.53	6.01	0.98
353	3.80	5.49	3.24
354	4.53	5.54	2.88
355	3.84	5.57	2.69
356	4.15	5.65	2.24
357	4.17	5.79	1.62
358	5.26	5.60	2.51
Mean	4.49	5.71	1.96
Median	4.15	5.65	1.86

Climax, 1981

Sample Number	Conductivity Micromhos Cm^{-1}	pH	Concentration Microequivalents L^{-1}
359	1.99	5.70	2.00
360	3.20	5.37	4.27
361	3.01	5.36	4.37
362	2.62	5.44	3.63
363	3.32	5.38	4.17
364	2.95	5.47	3.39
365	3.04	5.40	3.98
Mean	2.88	5.43	3.69
Median	3.01	5.40	3.98