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Sulfur in Precipitation
Contribution to
An Alberta Sulfur Inventory

by
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ALBERTA DEPARTMENT OF ENVIRONMENT
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1. INTRODUCTION

1.1 General

The study of sulfate in Alberta precipitation began in 1966 as a result of an increased concern over the environmental impact of the rapidly expanding oil and gas industry in Alberta. Among the manifestations that caused this concern may be cited the decrease in sulfur deficiency in some Alberta soils and the marked reduction in hail activity in central Alberta with an attendant increase in the number of soft hail incidences since 1961. In order to investigate the role of atmospheric SO_2 and sulfate in precipitation mechanisms, a project was set up in 1966 to collect and analyze precipitation from central Alberta. This project was concluded in 1970, and subsequently, Hitchon and Summers (1) of the Alberta Research Council published results showing that most of the sulfate in rain and hail collected in central Alberta was of local industrial origin. Furthermore, the amount of sulfate in snow was shown to be small and close to expected natural background. From a sulfur budget around the Rimbey area, it was concluded that a substantial amount of the SO_2 emitted was deposited locally as sulfate by convective summer storms.

The importance of this work both to Alberta agriculture and to an understanding of the gas processing industry prompted Alberta Environment through the Research Secretariat to support a three-year continuation of this initial effort, which commenced operation December 1st, 1972.

In addition it became apparent in September, 1973 that investigations related to the uptake of sulfur by plants and soils were under way at the Department of Soil Science, University of Alberta. Discussions among Alberta Environment, the University of Alberta, and the Alberta Research Council led to approval of a coordinated research program. In this way the Alberta Research Council was able to develop an independent area of environmental sulfur research as well as maintain an active involvement with other research groups. For their part, the University of Alberta provided laboratory space for sulfur analyses while the necessary staff, equipment, and chemicals were supplied jointly. In an additional joint project, the Alberta Research Council carried out laboratory simulation of SO_2 uptake by soils, tree bark, and similar material. In 1975 this part of our combined research was carried out entirely under the auspices of the Department of Soil Sciences.

1.2 Analytical Procedures for Inorganic Sulfur Compounds in Precipitation

It is generally assumed that airborne sulfur compounds consist of SO_2 and H_2S , along with inorganic sulfates as particulate or aerosol. It is further assumed that upon incorporation in precipitation, and before analysis, SO_2 and whatever small amount of H_2S is present, are oxidized to sulfate ion. Thus the basis for two of the three methods currently used to estimate the uptake of sulfur compounds in precipitation, and indeed dry fallout as well, is the precipitation of BaSO_4 . Summers and Hitchon (1) employed a conductometric titration using barium trichloroacetate, for which a standard deviation of ± 1.6 percent at 6 mg/l sulfate was claimed. Walker (2) used a precipitation technique employing radio-barium. Initial work in our study was by the conductometric titration method; however, it was found to be extremely tedious. Following the summer of 1973, we adopted the more accurate and sensitive technique of Johnson and Nishita (3) as modified by J.M. Crepin of the University of Alberta, Department of Soil Science. This method involves the reduction of all inorganic sulfur compounds to H_2S and the subsequent determination of bismuth sulfide by an optical method. An accuracy of ± 0.05 mg/l sulfur at 0.1 mg/l is claimed for the method. Intercomparison of all three methods indicates that the assumption of the rapid conversion of SO_2 , H_2S , and all other sulfur-containing species to SO_4 is valid, since good agreement (± 0.1 ppm) has been obtained between the methods based solely on sulfate precipitation and the last-named reductive method.

With a view to eliminating the possible misinterpretation of results designated as parts-per-million sulfur as pertaining only to elemental sulfur, and in keeping with the actual chemical situation, we report our data as parts-per-million SO_4 -S.

1.3 Uptake of Sulfate by Sampling Containers

Because sample collection and analysis are separated by large gaps in time, as exemplified by storage times as long as six months even though in a frozen state, the question of possible loss on storage had to be considered. Dummy samples, of known concentration and indistinguishable by the analyst from proper field samples, were carried along through the entire time scale from collection to analysis. The results given in Table 1 suggest that any change in SO_4 -S concentration is unimportant at the levels tested.

Table 1.

Effect of Storage upon Sulfate-Sulfur Determination

(All samples stored 4 weeks at -5°C)

Sample No.	Prepared mg/l	Found mg/l
B-002	0.5	0.4
B-2316	0.1	0.1
B-2393	1.6	1.4
C-002	0.5	0.6
J-019	0.5	0.3
LC-017	2.0	1.6
PR-011	1.2	1.4
SL-009	0.0	0.0

2. RESEARCH REPORT

2.1 General

While the main emphasis of the present work was to have been a continuation of the precipitation sampling in central Alberta as initiated by Hitchon and Summers (1), it was recognized early that such data as would be collected in central Alberta would likely suffer in interpretation without comparison to similar information from locations outside the principal geographical area of interest. Fortunately, we were able to interest the Federal Atmospheric Environment Service in contributing rain and snow samples to our survey from their many meteorological stations throughout the province and its environs.

The organization of this research report is based upon the premise that its major assumed goal is an estimation of an average yearly deposition of $\text{SO}_4\text{-S}$ in terms of weight per unit area for central Alberta. Central Alberta is considered to be roughly that portion of the province between Edmonton and Calgary extending east of the Rocky Mountains for approximately 200 miles. With the above general theme in mind, our research activities are herein subdivided first according to the season of the year. Thus, we begin with a perspective of $\text{SO}_4\text{-S}$ in summer precipitation for the entire province. The $\text{SO}_4\text{-S}$ detected in summer precipitation in the Alberta Hail Studies area of central Alberta is then compared to similar data from the whole province. The same format is applied to the data available for winter precipitation. Our purpose in this approach is to delineate the industrial $\text{SO}_4\text{-S}$ component of total deposition.

At this point the various other physico-chemical measurements carried out on both snow and rain or hail are discussed as they relate to the $\text{SO}_4\text{-S}$ content of precipitation. This phase of our field work is then followed by an account of the various laboratory experiments which were preliminary to the major undertaking of 1975, namely an estimation of the $\text{SO}_4\text{-S}$ contribution to total deposition made by dry fallout of sulfur containing particulate matter. In this way we describe our attempt at an estimate of $\text{SO}_4\text{-S}$ deposition due to rain, hail, snow and dry fallout for central Alberta. A detailed view of each phase of this work follows.

2.2 Overview - Rain 1974 and 1975 Atmospheric Environment Stations - Alberta

To obtain the precipitation samples required for a survey of the entire province, the cooperation of the Federal Atmospheric Environment Service (AES) was solicited, since they maintain a large number of meteorological stations throughout the province and its environs. Because precipitation samples were also received from the AES stations located in central Alberta, it became possible to compare results derived from these AES precipitation samples with those obtained through our association with the Alberta Hail Studies Group and the Alberta Research Council Atmospheric Sciences Division.

The $\text{SO}_4\text{-S}$ results for rain samples submitted by AES weather stations over a two-year period are given in Tables 2 and 3. The same results are shown as bar graphs in Figures 1 to 10. Differences showed up between average values and the corresponding median. Since it is relatively easy to contaminate a sample at the parts-per-million level $\text{SO}_4\text{-S}$ while a low $\text{SO}_4\text{-S}$ result tends to reflect good sample handling technique, more significance has been placed on the median (that is, that value at which 50 per cent of the results lie below and 50 per cent above). Also, since the majority of the frequency distribution curves given in this report are strongly skewed toward low values, a single high result can have a strong effect on the average yet not affect the median particularly. The accent on median values is to be noted as a major change in emphasis from our March 1st, 1975 interim report. This is a result of one year's additional data and a closer appraisal of all the data presently on hand. The median values indicated on Figures 1 to 10 have been given geographical perspective in Figures 11 and 12 for 1974 and 1975. From these graphs a number of pertinent observations can be made.

If one assumes that identical care was taken in the collection of rain from both the southern and northern halves of the province, then it is noteworthy that rain occurring at stations distant from more heavily populated central Alberta is uniformly low in $\text{SO}_4\text{-S}$ content. In most instances the amount of $\text{SO}_4\text{-S}$ found in rain at these stations is remarkably similar to that found in fresh snow in spite of the fact that the meteorological and physico-chemical processes controlling incorporation of $\text{SO}_4\text{-S}$ prevailing during summer and winter are quite different. Furthermore, a value of 0.2 ppm $\text{SO}_4\text{-S}$ compares with a similar value found in hail occurring north of Edmonton in which low-level air from the northeast was the prevailing input (1). More recent information due to Nyborg, et. al. (4) also reports low $\text{SO}_4\text{-S}$ values

in precipitation in the northern half of the province. In this context it is surprising that the town of Fort McMurray also reported precipitation of low $\text{SO}_4\text{-S}$ content.

Also significant is the fact that amounts of $\text{SO}_4\text{-S}$ greater than the 1.0 ppm reported by Summers and Hitchon and deemed to be indicative of the waste gases of the oil and gas industry have been found in rain noticeably beyond the influence of such activity. Conversely some locations in the heartland of sour gas processing submitted rain samples which consistently contained a very low concentration of $\text{SO}_4\text{-S}$. Such locations as Pincher Creek and Rocky Mountain House are significant in this regard, while among stations having high $\text{SO}_4\text{-S}$ rains, Vegreville is most interesting because even snow samples from Vegreville analyze high in $\text{SO}_4\text{-S}$.

A reasonable theory may be put forward for the Vegreville situation. The soils of the area are of a highly alkaline solonchic variety. This is aggravated or caused by the presence of extensive groundwater discharge areas which, upon evaporation, leave considerable expanses of friable sulfate salts. These salts become windblown suspended particulate and subsequently are washed out by rain or settle elsewhere. Further work would be justified in the Vegreville area to test the validity of this hypothesis, particularly if some means of differentiating between gas plant $\text{SO}_4\text{-S}$ and similar local windblown material would follow as a result. Indeed, it has become obvious that little understanding of industrial input to ecosystems can be obtained without a knowledge of what constitutes the background contribution.

The high values observed in Calgary rain indicate only the poor choice of location for the collection of this type of sample. It is recommended that a second AES station be established in the Calgary area and that this station not be located between major runways of an international airport. In this context, the rather high median values obtained at the Edson AES station - values apparently indicative of the Whitecourt gas complex - would seem to temper the choice of Edson as a Canadian meteorological station contributing to a world-wide network responsible for baseline data on a variety of chemical constituents in the atmosphere, sulfur among them.

The high value for Medicine Hat, and also the 0.6 ppm $\text{SO}_4\text{-S}$ from Coronation, again support the contention that the oil and gas industry is not the only source of atmospheric sulfur compounds (compare Calgary as well). While it has been brought to our attention (5) that no bulk soil in Alberta contains a large enough concentration of sulfate to account for the quantities of that substance deposited in central Alberta, it is likewise incontestable that the

surface soils of Alberta from Coronation south through Medicine Hat are highly alkaline and contain in places, especially dried-up sloughs, commercial quantities of Na_2SO_4 .

Data supplied by Alberta Environment on the $\text{SO}_4\text{-S}$ component of randomly-gathered airborne particulate indicate that for the Brooks-Medicine Hat region up to 20 percent of the particulate load is sulfate, especially in the summer months July to October (6). This represents between 0.5 and 2.2 lbs sulfur/acre from dry deposition of what must be windblown surface material indigenous to the area, because both Brooks and Medicine Hat are so far removed from the possible influence of sulfur extraction gas plants. Documentation of the chemical content of dustfall throughout the province would be enlightening in this regard.

It is because of this potentially important contribution of local or windblown sulfate-soil to total sulfur deposition that we speak of sulfur increases due to human activity of all kinds rather than specifically implicating only sulfur extraction gas plants. As yet, it is plainly not possible to unequivocally differentiate gas plant $\text{SO}_4\text{-S}$ from all other sources of sulfur.

2.3 Sulfur in Summer Precipitation as Collected in the Alberta Hail Studies Project Area/Central Alberta

2.3.1 Introduction

By the summer of 1973, two years had elapsed since the final field work which resulted in the Summers and Hitchon publication entitled "Source and Budget of Sulfate in Precipitation from Central Alberta, Canada" (1). The results presented in that paper were thought to be sufficiently important to warrant the collection of further data, with the hope such additional information would provide a more sophisticated appreciation of the fates of anthropogenic sulfur compounds emitted from sour gas processing plants in central Alberta.

As in the work of Summers and Hitchon (1), major reliance for precipitation samples was placed upon the Alberta Hail Studies (ALHAS) network. This network consists of hundreds of residents within a 90-mile radius of Penhold who have been instructed to collect and submit rain and hail in a prescribed manner. In addition, three storm chase vehicles were directed throughout the network by radio command from headquarters once radar had

delineated the area of rain activity. During the summers of 1973 to 1975, over 4500 samples were analyzed for silver in order to evaluate the utility of cloud seeding as a hail prevention technique. Of these samples some 400 to 600 were selected for $\text{SO}_4\text{-S}$ analysis. The criteria used for sample selection were as follows: (a) sufficient sample for analysis (more than 5 mls.); (b) a particular sample had to be part of a larger group which could be used to define a storm in time and encompassing area; (c) visibly uncontaminated and having been an acceptable silver sample. Thus it is now possible to compare the $\text{SO}_4\text{-S}$ values derived from AES weather station samples from throughout the province and its environs (compare figures 1 to 12 with the values for the same parameter obtained from a locale of high industrial sulfur emissions, namely that contained within an approximately 90 mile radius of Penhold).

2.3.2 Results and Discussion

(Some of the information contained in the March, 1975 Interim Report is reintroduced below for ease of comparison with more recent data).

By way of introduction to precipitation in central Alberta, figures 13 to 15 illustrate the frequency of rain as obtained from ALHAS network reports for each of the summer seasons in 1973 to 1975. The number of reports correlates very well with the extent and intensity of storm activity as reported by AES weather stations situated in central Alberta (Table 18). That rainout is of overwhelming importance in central Alberta as an atmospheric sulfur removal mechanism is a remark which has received wide credibility (1). On the contrary, Nyborg, et. al. (4) suggested dry-fallout of sulfur compounds is more significant. Such assertions have as a major underlying premise opposite suppositions as to the frequency of convective storms in the energy corridor of central Alberta. Figures 13 to 15, however, document rain to be of variable occurrence and intensity. Subsequent discussion will demonstrate its geographical variability as well. Thus, if one applies the very charitable condition that at least 10 reports of rain constitute a bona fide storm, then Figures 13 to 15 indicate that out of each 3 1/2-month field season 1973 to 1975, there are the equivalent of 1 1/2-months of rain-free weather - at least! As some of these rain-free periods last for a week at a time, rainout can not be considered the major $\text{SO}_4\text{-S}$ removal phenomenon during these periods. As a matter of fact, rainout and dry fallout would appear to be of almost equal importance on this basis. This is the first documentation for

a point of view which has, until this time, remained only a reasonable supposition. Moreover, it can be additionally asserted that calculations of rainout and washout efficiencies about a given sour gas facility (1) using average rainfall, its average $\text{SO}_4\text{-S}$ content, and monthly plant SO_2 emissions, are absolutely meaningless because they do not explain what happens to SO_2 emitted during periods when it is not raining around the plant in question. Such a calculation can only be envisaged for single precipitation events where detailed meteorological data are available. If, as is assumed by Summers and Hitchon (1) and documented below, again for the first time, daytime winds in the project area predominate from the southeast during convective storms, then Rimbey plant emissions could conceivably come to earth far to the northwest of the plant during such convective storms and not within a 25-mile radius of the plant. In principle this is capable of verification, but the exercise hinges upon detailed study of individual storms.

In the Interim Report (March, 1975) a mean value of 1.0 ppm (mg/l) of $\text{SO}_4\text{-S}$ was proposed for 1973 rain and hail in the project area. As has been stated on an earlier occasion, for this kind of information mean values are probably not as meaningful as median values, especially when the concentration distribution of samples from any storm is usually skewed in favor of lower $\text{SO}_4\text{-S}$ values. The average is always biased by a relatively few high results which are of dubious quality.

Although some emphasis was placed on the contention that the average value 1.0 ppm $\text{SO}_4\text{-S}$ calculated for 1973 rain and hail was apparently not materially different from that for the period 1967 to 1970, our reevaluation of the 1973 data along with the new 1974 storm data indicates that this is not true. On the basis of 157 samples representing 1973 precipitation, a median value of 0.7 ppm $\text{SO}_4\text{-S}$ may be compared with the lower median value for 1974 samples, 0.5 ppm $\text{SO}_4\text{-S}$. We feel that part or all of this decrease is attributable to improved techniques of sample collection as well as improved analytical procedures so that no real significance is attached to the slightly lower 1974 median. If the decreasing median values of Figure 16 do reflect improved plant efficiencies or tighter provincial air quality standards or both, support for these possibilities could only be obtained by a continuation of the present program. On the other hand, when individual precipitation events are compared, (Figures 17, 18, 22 to 24 for example) no significant changes in median $\text{SO}_4\text{-S}$ can be found to have occurred between 1973 and 1974. The information in Figures 17, 18, 22 to 24 relating

the particular 1973 and 1974 storms should be put into the perspective of their particular complete field seasons by additional reference to Figures 13 to 15.

Thus, each storm is described in terms of an improved bar graph particularizing the distribution of $\text{SO}_4\text{-S}$ values obtained from the storm (Figures 17, 18, 22 to 24). The same information is itemized geographically so that succeeding storms may be compared as to location and extent (Figures 19 to 21 and 25 to 30). In some cases the number of samples received from a given storm far exceeded our analytical capabilities. This necessitated choosing a limited number of samples for $\text{SO}_4\text{-S}$ determination. By indicating the total storm envelope as obtained from the total of all precipitation reports, it is possible to discern a possible 'location' bias in selecting samples for analysis. The storm extent derived in this way more accurately indicates whether succeeding storms overlap at all. This relates to the possible 'cleansing effect' of such successive events.

A descriptive history of the precipitation events of June 23, 24 and 29, 1973 as derived from radar echo maps of these storms accompanies Figures 19 to 21. These synopses indicate that each storm is a unique event to be researched as such. Only a comprehensive approach to individual events will advance over present level of understanding concerning the source and budget of sulfur in precipitation.

Each storm investigated differed in extent, intensity, and duration. In many cases more results were available for a particular township than could be accommodated on the displays of geographical distribution. However, it can be confidently stated that if a number of $\text{SO}_4\text{-S}$ determinations to be made from samples submitted from a given location (that is, the same township and range), all the results will be different. As this observation is contrary to what would have been anticipated, we feel the fact requires an explanation. Such an explanation is not to be found in this survey report. It is hopefully one of the purposes of this report to delineate subjects for possible future investigation.

As observed in the 1973 storms, the same range of $\text{SO}_4\text{-S}$ values is encountered no matter how large the area covered or how many potential industrial sources lie under the rain shadow: an increase of between 5 and 10 times in total sulfur emissions available to a storm does not change the median $\text{SO}_4\text{-S}$ concentrations observed, regardless of the extent of the storm envelope (Figures 17, 18, 22 to 24).

Benjamin (7), from a detailed study of surface winds as reported from Calgary, Rocky Mountain House, and Red Deer, concluded that within the region encompassed by these stations, surface winds often change in strength and direction (about 180 degrees) during the day. From midnight to noon a northwesterly flow of air due to cool air masses draining the mountains is followed during midday by a southeasterly system which may be the preferential direction feeding air to convective showers [compare above, and Summers and Hitchon (1)]. The extent and depth of this circulation pattern was shown to include most of the sour gas plants of interest. This system was also found to preserve its diurnal pattern to a depth of 1500 meters, with winds above this predominating from the west-northwest. Whenever plumes are trapped within this circulation system below 1500 meters, their residence time in the central Alberta energy corridor may be increased, and any expected pollutant concentration gradients would be smoothed out to provide a single uniform source of SO_2 upon which a storm might act.

Because the easterly extent of this circulation pattern was of importance to our study of sulfur compounds in dustfall, a similar cataloguing of diurnal winds was made for the Rimbey, Nevis, and Wimborne areas. In Figures 32 to 36 the northwest-southeast pattern is discernible for the Rimbey area. This places it also under the influence of the Rocky Mountains. However, this northwest-southeast pattern is weakened considerably by the time one proceeds 25 miles east of Red Deer (compare figures 31 to 36, Wimborne and Nevis) so that only SO_2 which has mixed with the upper (higher than 4500') westerly prevailing winds has a chance of deposition east of the sour gas corridor (that is, in the areas around Wimborne, Nevis, and beyond).

By sampling storms on successive days we were not able to detect any measurable 'cleansing' effect anticipated to take place under such conditions. Thus each storm must be considered as a single unique event. No further new conclusions may be gained from a continuation of the present survey approach to the fate of anthropogenic sulfur compounds. Average duration of rain and average amount of rainfall also provide no new insight into the reason for the $\text{SO}_4\text{-S}$ levels observed (Figures 22 to 24). Plotting the amount of rainfall reported against the $\text{SO}_4\text{-S}$ concentration of that rainfall for all samples processed only leads to the already well-known conclusion that there is a tendency for the $\text{SO}_4\text{-S}$ concentration to be inversely related to the amount of rainfall (Figures 37 to 39). This suggests a 'cleansing' effect during a given storm, but not for successive rains.

2.4 1974 Summer Field Project

As part of our commitment through the Environment Trust to cooperate with the Soil Science Group under Dr. Nyborg in providing an Alberta Sulfur Inventory, Mr. Barillot assisted in the construction, and then serviced, 14 field sites during the summer of 1974. Each site consisted of various types of exposed soil, alfalfa pots, constant-level water dishes, dustfall and liquid precipitation collectors, all within a 10 by 10 foot screened enclosure.

These sites required weekly tending to return rain and dust samples to Edmonton for analyses, and to maintain the required moisture content of exposed soils. In this way over 15,000 miles were logged from June to September, 1974. The 14 stations under our supervision were part of a larger network extending from Pincher Creek to Lacombe. Three additional stations were operated in the Tar Sands area. Data obtained from the above network will be found in The Alberta Environmental Research Trust supported project report "Fate of Emitted Sulfur Dioxide," administered by C.F. Bentley and M. Nyborg, and dated October 10, 1974. Our involvement consisted simply, therefore, of one technician for four months, plus some small advisory capacity on the part of the author, and the services of a Research Council vehicle.

Our involvement in this project was concluded at the end of the 1974 field season.

2.5 Sulfur in Winter Precipitation: 1973-1975

2.5.1 Fresh Snow

Freshly fallen snow was collected by Summers and Hitchon (1) in January, 1969, on two traverses between Edmonton and Vancouver, and at several locations in central Alberta. From the sulfate analyses of these samples it was concluded that: (a) the scavenging efficiency of snow is less than that of rain; (b) the amount of $\text{SO}_4\text{-S}$ contributed to snow by local anthropogenic sources must be less than 0.2 ppm (mg/l) in the vicinity of the Rimbey gas plant.

Because the above conclusions were based upon a very limited number of samples, and these from just two storms in January, 1969, a more complete census of $\text{SO}_4\text{-S}$ in snow for all of Alberta was attempted for the 1973-74 winter season. This survey was considerably simplified through the cooperation of 25 Federal Atmospheric Environment Service (AES) Weather Stations in and bordering Alberta, who sent us samples of fresh snow from each storm occurring at their location. This was an extremely fortunate maneuver as the 1973-74

snowfall was one of the heaviest on record and consequently provided the many sampling opportunities needed for a statistically meaningful analysis. Thus the 25 reporting AES stations submitted some 170 samples of fresh snow from throughout Alberta, along with results from what were intended to be reference sites in Fort St. John, B.C., and Fort Smith, N.W.T. A further 127 samples were received and analyzed during the 1974-75 winter as well.

The individual contributing stations and their analytical results are given as bar graphs in Figures 40 to 52 and tabulated in Tables 4 and 5. For each station, an average and a median $\text{SO}_4\text{-S}$ value were calculated. In so doing it again became apparent that, in general, the distribution of analytical results for the individual stations, as well as the total distributions depicted in Figures 53 and 54 were not symmetrical about the mean value. As a result, significant differences were noticed between mean $\text{SO}_4\text{-S}$ value and median values. After some deliberation it was decided that the nature of the data supported the median as the more meaningful variable. Our justification is again based upon the observation that we are dealing with extremely low concentrations of $\text{SO}_4\text{-S}$ and hence care must be taken in the handling and shipping of field samples. Consequently, a few contaminated samples can easily overbalance a lot of careful work. Our decision to use median values is not entirely incontestable but seems to be reasonable, based on our experience with the information and procedures in sample processing. Thus total frequency distribution bar graphs in Figures 53 and 54 indicate that the average $\text{SO}_4\text{-S}$ content of fresh snow has increased from 0.4 ppm in 1973-74 to 0.8 ppm in 1974-75, whereas the median value remains 0.2 ppm. A partial explanation for the increase in the 1974-75 average is the large number of samples containing very high $\text{SO}_4\text{-S}$ received from Vegreville (Figure 52). Certainly during the much heavier 1973-74 snow conditions, Vegreville results were more in line with those of other localities reporting. At any rate, further reference to rain data (Figure 10) for Vegreville indicates that explanation of these high values would probably aid immeasurably in isolating the various sources of $\text{SO}_4\text{-S}$ mentioned in this report.

As a total frequency distribution obscures the possible regional variations which are also data of interest in this report, such regional information is given graphically in Figure 55 for the 1973-74 winter and in Figure 56 for the 1974-75 winter.

2.5.2 Fresh Snow - Discussion

The contribution of $\text{SO}_4\text{-S}$ from the world-wide background is not known for snow, but is probably much less than that in rain (~ 0.3 ppm) for two reasons. First, the scavenging efficiency of snow is less than that for rain, since the liquid water content of snow-producing clouds in Alberta is about one-tenth that of summertime cumulus. In addition, the rate of SO_2 uptake on snow crystals would be expected to be much slower under winter temperature conditions. For these reasons it may be concluded that the amounts of $\text{SO}_4\text{-S}$ found in fresh snow collected during the 1973-74 winter would also be very small and so close to expected natural background that it would be impossible to determine from fresh snow how much sulfur is of local origin. In addition, much of Alberta's snow originates in Arctic air masses which pass over areas essentially devoid of any human activity. Hence one can imagine clean snow-producing air masses passing from the west-northwest through Alberta under relatively stable meteorological conditions with little vertical transport of air. In this situation SO_2 would be trapped in the lowest few thousand feet of the atmosphere with little chance to participate in the precipitation mechanism. This hypothesis is amply supported by the uniformly low values of $\text{SO}_4\text{-S}$ in fresh snow. These conclusions are in accord with the less fully documented suggestions first put forward by Summers and Hitchon (1), and earlier by Don Walker (2), both papers indicating Alberta anthropogenic sulfur in fresh snow between 0.2 to 0.1 ppm with an uncertainty of ± 0.05 ppm.

Although the median values as depicted in Figures 55 and 56 indicate that $\text{SO}_4\text{-S}$ content of fresh snow is generally lower than that observed in rain and hail, and indeed fresh snow samples we have collected ourselves support this low value, enough instances of higher amounts of $\text{SO}_4\text{-S}$ in individual samples submitted by AES stations prompts us to look for explanations for these high values which do not impute faulty technique to the collection personnel. The scope of the present work can only be considered as the survey work which directs attention to topics warranting future detailed study. Intensive study of single events will be the most fruitful approach to research arising from this report.

Survey work of the type described and carried out under this contract obviously has depended upon the cooperation of a number of different groups; in the case of the collection of precipitation, the value of the AES contribution is immeasurable. This organization is able to provide survey-type

information on a large geographical scale. The importance of information available from such stations makes it necessary that these stations be located in areas free from unusual local disturbances. By way of example, it is realized that necessity requires the location of meteorological stations at airports. All $\text{SO}_4\text{-S}$ data from the Calgary AES station which is located between major runways of the International Airport, is, because of this fact, essentially useless. Certainly this study further indicates considerable information can be derived from such stations if the station is properly sited and the staff made aware of the importance of their efforts in collection and handling of precipitation samples.

2.5.3 Winter 1973-74 - Total Snowfall

The extremely low values obtained for $\text{SO}_4\text{-S}$ in fresh snow suggest that in winter anthropogenic sulfur is dispersed on a grand scale and in low concentration downwind from emission sources. Such a conclusion is hasty because in sampling only freshly-fallen snow the possible importance of wintertime dry fallout of particulate sulfate is overlooked as is the possible contribution of slow adsorption and subsequent oxidation of gaseous SO_2 upon snow lying on the land for extended periods.

Again, the ample total fall of snow which took place during the 1973-74 winter provided an excellent opportunity to ascertain the importance of these possible additional contributions to $\text{SO}_4\text{-S}$ over that found in fresh snow. The very large depth of snow along with the fact that temperatures remained below freezing throughout the winter assured that loss of $\text{SO}_4\text{-S}$ due to solution and migration through the snow pack would be a minor concern. Any contribution from indigenous blowing soil and high sulfate content, a concern in summer, could also be ignored. Thus the sulfur content found in the total depth of snow would be a measure of the wintertime contribution of purely anthropogenic sulfur to the land surface sampled.

The winter situation is also of interest from the total air pollution point of view since it is evident from a perusal of monthly sulfation cylinder data that significantly higher sulfation values are obtained during winter months than during the summer (up to 10 times on occasion) (data supplied by Air Pollution Control Branch, Alberta Environment, November 23, 1972) Consequently, in February 1974, we sampled what amounted to a 3 1/2 month accumulation of snow both up- and down-wind of three sulfur extraction gas

plants in central Alberta. The samples were taken in a direction consistent with the general west-northwest origin of winter weather systems.

The results are tabulated in Table 6, presented as a bar graph in Figure 57, and shown in their geographical distribution in Figure 58 as pounds of sulfur per acre contributed to the land during the 3 1/2 months covered in the sampling. The latter results were obtained by converting the volume of snow sampled to liquid water and thus are a measure of anthropogenic $\text{SO}_4\text{-S}$ deposited from November 1st, 1973 to February 13th, 1974.

Over the approximately 150 miles downwind and 30 miles upwind of the sulfur extraction gas plants circled in Figure 58, no simple radial distribution of sulfur is evident. Perhaps a larger downwind sampling path would have indicated some trend. However, it is evident that, given a median value of 0.2 ppm sulfur in freshly-fallen snow, accumulated snowfall contains between two and three times that concentration of $\text{SO}_4\text{-S}$, a factor which indicates that wintertime dry-deposition is of at least equal importance as snow-out for the deposition of sulfur-containing compounds.

If a median value of 0.4 lbs sulfur per acre is taken as representative of winter deposition on the land, and not just as potential spring runoff, then this 0.4 lbs/acre over a 3.5 month winter period may be combined with the June-August estimate of sulfur from convective storms [0.8 lbs per acre in the Rimbey area (1)], and also with what this study considers as the amount of anthropogenic sulfur in dustfall to yield a total yearly average value for anthropogenic sulfur deposited in an area of approximately 15 townships by 15 ranges (8100 sq. mi.) in central Alberta, having township 41 Range 27 W 4 as its center. Table 7 displays this accounting and the total of 1.9 lbs of $\text{SO}_4\text{-S}$ per acre, a figure to be compared with average annual application required of 10 lb of sulfur per acre (8). This is obviously not the type of comparison which can placate the individual farmer convinced of economic and bodily ruin at the hands of the sour gas industry. Nor does this study purport to consider the problem of sulfur in precipitation at this micro-scale, even though it may be the more important one to solve.

The simple accounting for sulfur given above also makes clear that the amount of $\text{SO}_4\text{-S}$ deposited in rain is approximately equal to that brought to earth through dry deposition. In other words, these two deposition mechanisms are roughly of equal importance in Alberta, as has been shown to be the case in eastern Canada and the United States (9, 10). Thus, Alberta is probably not the 'special case' it was previously thought to be in which dry deposition was promoted as the most important deposition mechanism. This

condition may prevail in special regions such as the Pincher Creek area, but it certainly does not appear to be the case in central Alberta.

Table 7 Total Yearly Average SO₄-S Deposition

	<u>lbs SO₄-S/acre</u>
Snow (November 1st-February 13th)	0.4
Rain (June-August)	0.8 2.3
Dry Fall-out (May-November)	<u>0.7</u>
	1.9 lbs SO ₄ -S/acre

When confronted by data in terms of lbs of sulfur per acre in an area downwind of sulfur extraction gas plants, it is tempting to relate the plant output to some integrated amount of sulfur deposited over a certain specified area. We shall perform the exercise, then delineate its rather obvious shortcomings: we use the total emissions for the months November 1st, 1973, as they pertain to the Texaco Bonnie Glen gas plant, the Rimbey gas plant, and the two Nevis gas plants. These data were obtained from the Energy Resources Conservation Board, Calgary, and are reproduced below.

Table 8 Sulfur Emissions from Selected Gas Plants
November 1, 1973-February 13, 1974

<u>Plant</u>		<u>Long Tons Sulfur Emitted November 1st, 1973 - February 13th, 1974</u>
Bonnie Glen	(S 1/1 17-47-27-W4)	635
Home Glen Rimbey	(S 1/2 5-44-1-W5)	1910
Chevron Nevis	(SE 1/4 22-39-22-W4)	377
Gulf Nevis	(NE 1/4 33-38-22-W4)	<u>989</u>
		<u>3911</u>

This amount of sulfur could be spread over an area of 16,000 square miles (a rectangle 225 by 70 miles lying along a north-northwest - south-southeast axis) at the uniform rate of 1 lb of sulfur per acre. Such an application is near the maximum level depicted in Figure 58. This type of calculation would suggest that if the sources of sulfur are only those chosen above (and circled in Figure 58), it is entirely possible that even in

winter most Alberta-generated sulfur emissions are deposited within the given area downwind of the source; with the parameters chosen this would be an area still within Alberta's borders.

Since this type of calculation is so sensitive to the parameters chosen, it is of little value. It is not known, for example, whether only the plants indicated contribute to the $\text{SO}_4\text{-S}$ deposited. Also, the deposition of sulfur is not likely uniform over the arbitrary area chosen and we do not have the financial or physical capabilities to construct isopleths from which to make more accurate integrations. Without simultaneous determination of atmospheric SO_2 and H_2S concentration isopleths at long distances downwind from potential sources, we cannot presume such concentrations to be once again background level. As a matter of fact, we do not know what constitutes an Alberta background level for any of the suspected pollutant currently monitored by the province.

2.6 Other Physico-Chemical Measurements Related to 1973-75 Precipitation

When sufficient sample was available, the hydrogen ion concentration (acidity) was determined and recorded as $\text{pH}[-\log(\text{H}^+)]$. In addition, the specific conductance was also measured. The latter provided information on the total number of ions in the sample in question, which could then be compared to the amount of sulfate and the pH. In cases where the observed hydrogen ion concentration is equal to twice the sulfate ion concentration, the tendency is to conclude that sulfuric acid is present in the sample. The concern, then, is not the $\text{SO}_4\text{-S}$ value per se but the fact that under the proper conditions SO_2 dissolved and oxidized in precipitation produces sulfuric acid which is potentially capable, when present in sufficient concentration, of altering soil pH and subsequently the type of vegetation such soil will support.

Specific conductance and pH of selected samples are included in Tables 9 and 10. At any given station, pHs and specific conductance were not constant but varied from storm to storm, the variation in pH being as large as 1.5 pH units; thus for rain at Rocky Mountain House on August 18, $\text{pH} = 6.2$ (slightly acid) but on September 29, $\text{pH} = 7.7$ (slightly basic). In samples for which pH, specific conductance, and sulfate concentration information was obtained, there was no obvious relationship between these variables. Perhaps if these samples had been analysed for the cations Na^+ , Ca^{++} , Mg^{++} , and K^+ , these inconsistencies might make more sense, as both

pH and specific conductance are influenced by the relative abundance of alkali and alkaline earth cations.

The same general conclusions have been found to apply to snow samples as well (see Table 9).

Table 11 Sulfate-Sulfur, pH and Specific Conductance
for Selected Fresh Snow Samples, 1973-74

<u>Date</u>	<u>Location</u>	<u>(S)ppm</u>	<u>pH</u>	<u>Sp. Cond. (μ mhos)</u>
February 27	Coronation	0.2	6.0	---
March 13	Coronation	0.5	7.1	---
February 12	Lacombe	0.2	5.6	---
March 17	Rocky Mountain House	0.3	4.8	10.5

What is extremely significant in the data displayed in Tables 9 and 11, is the inference that it is possible for snow to exhibit acid pHs. Of course, whether this effect is ever transmitted to the frozen soil underneath is not known at this time. This acidity no doubt manifests itself somewhere in the sulfur cycle, most likely in the spring runoff to local water courses. It may also be pointed out that for the March 5 Rocky Mountain House data above, a pH = 4.8 is very close to what one would expect for an aqueous solution of sulfuric acid containing 0.3 ppm $\text{SO}_4\text{-S}$. Hence, one may infer that this particular snow contained sulfuric acid as the major contaminant. Occurrences of acidic precipitation may be generally more prevalent in winter than summer because of the lower particulate loading of the atmosphere, particularly where that particulate is composed of neutralizing cations such as Na^+ , K^+ , Mg^{++} , and Ca^{++} . Once again these measurements that have been made point to possible areas for future expanded investigations.

The pH of rainfall in the absence of any foreign influences should approximate that of a saturated solution of CO_2 , namely a pH of 5.5. Examination of the results in Tables 9 and 10 indicates that, with one or two exceptions, the measured pHs of rainfall and fresh snow are greater than 5.5, that is, more basic. This situation prevails regardless of the $\text{SO}_4\text{-S}$ content of the sample in question (compare entries in Tables 9, 10, 11). The suggested meaning of this observation is that the rainfall collected contains sufficient basic equivalence to titrate or neutralize a saturated CO_2 solution, plus any additional acid equivalence associated with the solubility of SO_2 in rain.

How much particulate material would produce such a change of pH? A few simple but reasonable assumptions can be made which suggest a rather unexpected answer to the above question. If one assumes the particulate to have an average molecular weight of 100 and one basic equivalent per mole, then for a rainfall of 0.2 in. (2.5 mm) falling through 1000 m of air, only 60×10^{-8} gm of particulate per cubic meter would produce the indicated pH change. This is a particulate loading 100 times lower than the present provincial allowable for suspended particulate ($< 60 \times 10^{-6}$ gm/m³ as an annual mean)! One would almost be led to believe that the material which causes nucleation of a raindrop, in Alberta at least, is sufficiently alkaline to increase the pH change from that of the CO₂-H₂O equilibrium.

Although we have no elemental analyses of rain water, metal analyses of dustfall indicates high sodium, calcium, iron, and phosphorous in the H₂O soluble fraction. The presence of phosphorous, particularly if in the form of phosphate, would supply the weak acid anion needed to explain the rise in pH. Such an anion would also provide buffer capacity to maintain the pH in the range observed. Actual analyses of rainwater are obviously necessary in order to test the above postulates.

Finally, Whelpdale and Summers (11) point out that rain collected in eastern Canada is always of a pH lower than 5.5, sometimes as low as 4.0. Because of this fact, it has been thought that faulty technique, which allows considerable particulate contamination of our rain samples, caused the pH of Alberta rain to be greater than 5.5. However, because of the above calculation, the apparent alkaline nature of our suspended particulate, and the fact that high pHs have been observed for rain samples having specific conductances of the same order of magnitude as good distilled water (that is, less than 10 µmhos), we are inclined to rule out faulty technique as a viable explanation. The observation of pHs greater than 6, demonstrated in this work for Alberta rainfall, including that collected in central Alberta, must also be reconciled with the observations of Nyborg et al. (4) in regard to decreases of pH in test soils also located in central Alberta. Finally, Brosset (12), in a study of precipitation in Sweden, observed that precipitation occurring in nonindustrial areas is characterized by pHs in the range 5.5 to 7.0 whereas rain in highly populated industrial regions always is of a pH lower than 5.5.

2.7 Uptake of SO₂ by Soils, Water and Tree Bark - Laboratory Simulation of Field Experiments

Analyses of exposed materials from field monitoring stations, under the general supervision of M. Nyborg, University of Alberta, Department of Soil Science, showed that large amounts of airborne sulfur compounds may be taken up by soil, water, tree bark, and plant detritus (4). To supply more backup information on SO₂ uptake by the biosphere under controlled atmospheres, an environmental chamber was constructed at the Research Council. Soil samples, identical to those exposed at the field stations, constant-level water dishes, tree bark, and forest litter were maintained for various periods of time at controlled humidity, air flow, and SO₂ level so that adsorption of SO₂ could be quantified. pH changes were also noted.

Tables 12, 13 and 14 summarize the findings, each entry representing the average of duplicate samples and analyses. The concentrations of SO₂ and the length of the experiment were chosen so as to bear a reasonable relationship to the various Alberta Maximum Permissible Concentrations of SO₂ in ambient air, which are:

- (a) 12 ppb as an annual arithmetic mean
- (b) 58 ppb as an average 24 hour maximum.

24 ppb for 30 days was the lowest experimentally attainable SO₂ concentration with the existing apparatus.

Unfortunately, no measure of actual average field concentrations of SO₂ are available with which to compare the laboratory results. Nevertheless the results do substantiate observations from similar field experiments: namely that large, reproducible amounts of SO₂ are absorbed by soils - as much as 1.2 lbs. SO₄-S per acre in the case of a constant 24 ppb SO₂ over a 30-day period (Table 13). Additionally, a corresponding drop of about 0.1 pH unit is also evident in both the simulated and field experiments (Table 14). The large decrease in the pH of distilled water compared to the 0.1 pH unit for the typical soils is also very evident and supports for example, the great concern the Swedish Salmon Fishery has shown over the decrease in salmon productivity in that country and its relation to increased acidity of lakes and streams, even though under more severely stressed conditions than exist here. Our result also dramatizes the possible effect of even parts-per-billion levels of SO₂ on the pH of natural water courses unless sufficient buffering capacity is present (as presumable is the case in soils where roughly comparable increases in SO₄-S produce only 0.1 pH unit changes).

In 1975 responsibility for further work in this area was given over to the Nyborg Group in the Department of Soil Science at the University of Alberta.

2.8 The Accurate and Reliable Determination of SO₂ Concentrations in the Parts-Per-Billion Range, 1973-75

One aspect of sulfur emissions which has received little local interest is the persistence of SO₂ outside of defined plume boundaries, that is many miles from sources. The measurement of such concentrations has relevance to a variety of issues. One issue is the problem of the continued increase in SO₂ background levels over the northern hemisphere and the potential effects on a worldwide level of such an increase. A second issue concerns the possibility, nay the probability, that under certain meteorological conditions, Alberta emissions come to earth beyond our borders.

From the geographically widely scattered profiles that are available, SO₂ concentrations below 10 ppb (parts-per-billion, v/v) are anticipated for 'clean' air. Given a background value of 2 ppb, a lifetime for airborne SO₂ of approximately 40 days may be calculated. On the other hand, should the background be closer to 0.2 ppb, a value of 4 days would be a reasonable half-life, depending, of course, in both cases on the removal mechanism. Most estimates to date range from 2 to 7 days. A need for SO₂ measurement capability in the fractional part-per-billion range was identified as an important aspect of our program.

This program, begun in October, 1973, established the analytical basis for all SO₂ measurement techniques. Equipment incorporating gas permeation tubes was constructed for the preparation of known low (<1 ppm) concentrations of SO₂, H₂O, NO₂, and NH₃. This apparatus provided the means whereby commercial-type SO₂ monitors could be maintained in calibration.

A critical evaluation of such commercially available SO₂ monitors indicated that none was reliable below 10 ppb SO₂, a regime judged to exist the majority of the time outside plume infringement zones. Correspondence and discussion with leading atmospheric scientists suggested the West-Gaeke colorimetric procedure as the most reliable below 10 ppb SO₂.

This method was therefore adopted and the equipment and techniques peculiar to its use were perfected by both laboratory and field studies. With reasonable care, less than 5 ppb SO₂ can be determined to a routine accuracy of ± 10 percent in a 30 l sample of air. Moreover, it was shown

that the commercial instruments inherited from the original vote holder were awkward to use, not sensitive enough, and not properly calibrated for the measurement of ground level SO₂ concentrations during convective summer storms, the job for which they had been purchased.

The accepted procedure used for deriving tropospheric SO₂ lifetimes downwind from a particular source is to fly at a number of radial distances from the source, 5, 25, 50, 100 mi., for example. At each radius SO₂ measurements are taken along with the measurement of some variable which decays by dilution and only very slowly or not at all chemically. A comparison of SO₂ to the dilution component at each radius then affords a measure of the chemical decay of SO₂ and from this an SO₂ half-life is derived.

As dilution markers, both condensation nuclei and CO concentrations have been used. We purchased a commercial condensation nuclei counter for this purpose and have completed the construction of an instrument which is capable of CO measurements below 0.2 ppm, a range which is expected to prevail over Alberta.

A trial flight was made in October, 1974. Fort McMurray was the site chosen because of the high emission levels expected from the sulfur plant and the steam-generating facility in comparison with the rather stricter emission controls in populated central Alberta.

The experimental conditions in Table 15 prevailed.

Table 15 Airborne SO₂ Sampling Parameters. Fort McMurray, Alberta

	2 October, 1974
Barometer:	29.39" and clear
Wind	West @ 24-30 mph
Air Temperature	8°C
Altitude Flown	2200 ft. 5 and 10 mi from plant
	3000 ft. 35 mi from plant

West-Gaeke samples at 5, 10, and 35 miles from the source showed no detectable SO₂, although 10 ppb could easily have been separated from background. Because a commercial SO₂ instrument in parallel with the colorimetric West-Gaeke apparatus recorded above threshold (5 ppb) our sample collection efficiency was called into question. Subsequent comparison with

an Alberta Environment owned Phillips SO₂ analyzers failed to settle the question. Consequently, an improved laboratory source of ppb levels of contaminant would be a very valuable facility to the growing community of environmental monitoring laboratories in the province. The expanding list of chemicals whose toxicity is discernible even at the parts-per-billion level - nickel, carbonyl, and beryllium being outstanding examples - certainly prompts serious consideration of such a control calibration facility somewhere in the province.

In this context, an apparatus was constructed with the purpose of producing ppb levels of SO₂. The inability to maintain a constant level of SO₂ in the range desired caused abandonment of our active involvement in the project. However, because its importance was strongly felt, Research Council funds were subsequently used to support Dr. Walter Quiring of Western Research and Development Ltd., in the preparation of a state-of-the-art review concerning the subject of ppb gas calibration mixes (13).

It is hoped that this information will be made available as an ARC Information Series Publication to those interested enough to pursue the matter further.

2.9 Central Alberta Dustfall Survey

2.9.1 Introduction

Previous work by ourselves (14) indicated that at least for the Lacombe area in 1974, as much sulfur could be accounted for as dry fallout as came down in summer rain and hail. On the contrary, M. Nyborg, et al., (4) have suggested that Alberta differed significantly from eastern Canada and the United States where precipitation has been reported to be the major mechanism by which atmospheric sulfur is scavenged to earth.

The validity of these Alberta-generated conclusions regarding the significance of the dry sink is heavily predicated upon sulfur uptake by soils and crop-test-plots around the Waterton sour gas processing plant, where surface wind patterns are well-defined and well-behaved at least to the mesoscale investigated (~20-30 miles downwind). Supposed additional confirmation for the apparent importance of dry fallout of sulfur species arises from the analyses of a variety of biological and instrumental sulfur monitors maintained at sites near and remotely (greater than 60 miles) east of the major anthropogenic sources in central Alberta; however in this case the evidence is open to question.

Because the amounts of sulfur apparently taken up by the above mentioned sulfur monitors substantially exceeded that amount expected from a simple advection/diffusion model applied to sour gas plant emissions, it was thought advisable to reexamine the basic premise; namely, that it is possible to relate present amounts of sulfur in central Alberta dustfall to emissions from sour gas processing plants located between Red Deer and Calgary and predominantly west of highway 2. A further impetus was given the present study by the lack of statistical validity associated with previous studies concerned with the role played by dry fallout as a sulfur sink in central Alberta, particularly as results regarding its importance are at variance with findings from other parts of the world (10). It is therefore incumbent upon us to describe in some detail our experimental procedures as well as our data reduction methods.

2.9.2 Experimental

1. Location of sampling domains. Initially, it was decided to select three basic sampling areas, each 12 miles in east-west extent by 30 miles in north-south dimension (that is, two ranges by five townships). These are shown in Figures 59 and 60. Their choice was determined by the following considerations:

- a) The Rimbey area selected was already intensively instrumented and researched by the Alberta Hail Project group (a creation of the Weather Modification Board and the Alberta Research Council, Atmospheric Sciences Division). That rain and hail samples as well as meso- and micro-scale meteorological information were available for these two ranges by five township domain determined the size of the remaining two sampling domains. Although a similar sized tract immediately east of the presumed downwind direction of the large Rimbey gas plant would have been more desirable, the townships adopted did include at least three sour gas processing facilities which, while not large enough to recover elemental sulfur, burnt their H_2S at flare. Fortunately local surface wind data were available from the Homeglen Rimbey Gulf mobile monitoring trailer (Figures 32 to 36).

- b) Since other sulfur research groups had already set up sites along specific north-south lines east of highway 2, it was appropriate to also locate our sampling domains in accordance with these established distances, and thereby facilitate intercomparison of data.

Subsequent to the choice of domains, each township was considered as a 6 by 6 grid. Using random-number tables, two sampling stations were selected in each township by choosing pairs of "x" coordinates and their "y" counterparts, each as a random number from 0 to 6 representing the number of miles on each side of a township. In this way each township was represented by two randomly sited dustfall monitoring stations located at the indicated (x, y) map coordinates. Twenty sampling sites for each large sampling area and a total of 60 random sites in all were established. Thus, where in previous graphs of sulfur deposition versus distance from some assumed source, no confidence limits of any sort were given for individual data points, our approach would now, hopefully provide the much needed measure of reliability in experimental sulfur values for each of the three sampling domains.

2. Factors governing design of the Dustfall Collector. The collection and analysis of dustfall is an integral activity in the characterization of environmental quality, especially for urban areas. As such, much attention has been given to the establishment of uniform operating standards for the measurement of rate of dustfall (15 to 18).

Accordingly, each sampling station consisted of a slightly tapered polyethylene container 10.5 cm in diameter at the top and 16 cm in depth. This was snugly fitted inside a metal holder which in turn was set at a height of 2.5 m (8 ft) above open ground such that the top of any higher object in the vicinity was much less than the recommended 30° above the sampling point. All sampling sites were Zone G (15) - rural, one dwelling limit per 5 acres or larger area. Each container was provided with 25 ml of 0.04 percent w/w of Dowicide-B to inhibit algae growth.

Two additional sampling sites were maintained on Research Council premises in Edmonton. Each of these stations consisted of two containers - one of ours and a second obtained from Alberta Environment. In this way it was possible to confirm that, within experimental error, no difference in collection efficiency could be observed between our containers and those used by Alberta Environment, even though there was a slight difference in geometry.

Although various types of shields designed to reduce vertical wind eddies in the mouth of the gauge are available, Nader (16) has demonstrated by the use of "doped" gauges that the retention efficiency of the simple collectors such as we and Alberta Environment use is close to 100 per cent in winds up to 20 mph. As accompanying wind diagrams (Figures 31 to 36) attest, winds in the test areas rarely exceed this velocity. Furthermore, Nipher and Alter shields are normally reserved for snow collectors, because snow, being light, is more susceptible to re-entrainment. Above all, it must be emphasized that a dustfall collector measures the quantity of material which will settle on a horizontal surface; it does not attempt to describe the total particulate burden of the atmosphere. This point is crucial to the interpretation of dustfall data.

As additional support for the use of polyethylene dustfall gauges, Nader (16) has observed (and our practical experience confirms) that polyethylene containers may have superior dust retention because of the static electric charge which builds up on the inside walls.

3. Sample collection and treatment. The dustfall gauges were changed on a 30-day basis, care being taken to avoid the introduction of extraneous material, particularly of a sulfur-containing nature. The analytical procedure was essentially that described in (15) and (18). At least six blanks were carried through with each month's batch of field samples in order to determine a probable analytical error for the processing of a single sample. We were able in this way to develop a probable error in the evaluation of the water insoluble material (± 0.7 mg); and for the water soluble material the blanks were used to establish the weight correction of the Dowicide B ($4.1 \text{ mg} \pm 0.7 \text{ mg}$) added initially to each dustfall cannister in the field.

Soluble sulfate analyses were by the modified Johnson-Nishita method (3). Once an aliquot of the water-soluble material was removed for sulfur analysis as above, the remainder of the water-soluble fraction was evaporated to dryness at 105°C weighed, and then sent to Barringer Research of Toronto for further elemental analyses. The water-insoluble material was also sent to Barringer for similar analyses.

On two occasions sulfur analyses were carried out at Barringer Research on the dried residue from the water-soluble fraction. The method involved the dissolution of the residue in perchloric acid followed by the nephelometric determination of sulfur in a stabilized BaSO_4 suspension. The sulfur values thus obtained were expected to agree with those obtained by the Johnson-Nishita method. This was not the case, unfortunately. The Barringer results were always lower by a factor of 20 to 50. Lengthy discussion

with both analytical services failed to resolve the discrepancy, so the Johnson-Nishita results have been used throughout since it was more realistic to err on the positive side with regard to the sulfur deposition rates derived from the data. Moreover, some measure of confidence has already been established for the Johnson-Nishita method by ourselves, Dr. Nyborg's group, and Don Walker at Lacombe. Nevertheless, it is recognized that some method of quality control and intercomparison between laboratories of standard samples is of the utmost urgency before any sulfur data can be discussed with total confidence.

As previously mentioned, multi-element analyses were done on both the water-soluble and the water-insoluble fractions of the dustfall in addition to the sulfur determinations. Simultaneous analyses for 22 elements were obtained on each sample using a radio-frequency argon plasma emission spectrometer. This was done under contract by Barringer Research of Toronto.

Additional characterization of the water-insoluble material resulted from X-ray diffraction studies of selected samples.

Because Dr. Krouse of the Physics Department of the University of Calgary has had some success in suggesting possible origins of sulfur species given the relative isotopic sulfur abundance present in a sample, a selection of samples was sent to him for S^{34}/S^{32} measurement and interpretation. These results will be discussed below.

4. Data Reduction. Laboratory work-up of each month's sample from the field yielded tabulations of individual total dustfall rates as well as sulfur deposition rates for all 20 stations in each sampling domain. From these results calculations of a "monthly mean" total dustfall and a monthly mean sulfur deposition were made. The computational procedures were those described in references (15) and (17), wherein the log-normal distribution of measurements of particulate deposition had been reconfirmed. With this statement, we imply that all experimental data are converted to logarithmic form which are then used in "plug-in" formulae described in most basic statistics texts. Thus values of total dustfall rate and sulfur deposition in Figures 61, 62, and 63, are obtained as geometric means with the upper and lower boundaries indicating 95 per cent confidence limits for the means so calculated.

Moreover, the formula

$$N = \frac{(C.V.)^2 t^2}{p^2}$$

where:

N = minimum number of stations required
 t = student "t" for specified confidence
 C.V. = Coefficient of variance in percent

$$\frac{\text{Std. Dev.}}{\text{Mean}} \times 100$$

p = allowable percent departure from
the true mean

has been employed to additionally establish that by using the data from only 15 of the 20 stations in each domain we are still 95 percent sure that the mean values calculated and shown in Figures 61, 62, and 63 do not differ from the true mean by more than 10 percent. This ploy allows us to apply Grubb's interative rejection criteria to the raw data in order to reject results greater or smaller than a prescribed fraction of the mean and still have sufficient data from which to calculate a 95 percent reliable mean rate of dustfall or sulfur deposition.

In summation, then, the monthly data points of Figures 61, 62, and 63, are geometric mean values for which we are 95 percent certain that the true mean lies within the limits given. In addition we can say that even after applying data rejection criteria, information from enough sampling stations is still available in each domain to declare the calculated means to be not more than 10 percent from what could be termed the "true mean" (17).

2.9.3 Discussion of Results

As with any measurement, a proper interpretation of its significance rests ultimately upon an understanding of the measure itself. It is our opinion that large portions of what are held by the nonexpert to be reliable and reputable conclusions are based upon measurements whose limitations are not as widely reported as the conclusions derived therefrom.

With regard to the data whose derivation has been outlined immediately above, the intent of this measure is to describe the mass rate of fall of particulate matter. It measures the quantity of material that will settle on a horizontal surface. The total particulate or dust content of the air is not measured; nor will this type of test determine the rate of emissions from suspected sources. Because of its settleable nature, the origins of the material captured by the dustfall gauge are predominantly within a 5-mile radius of the individual gauge or collector. This, however, is not to imply that suspended material whose source may be gas plant emissions is not to be picked up - only that the amount of this material will be some fraction of the total and at the present stage of experimentation indistinguishable as to origin from all other sulfur species collected.

A rather substantial size differential exists between the cross-sectional area of the dustfall container used in the field and the conventional units expressing the amount of material deposited as dustfall. Thus Figures 61 to 66 indicate deposition in terms of kilograms per hectare. The usual dustfall container has a cross-sectional area approximating 10^{-2} square meters, whereas one hectare represents 10^4 square meters. A million-fold extrapolation in area is thereby necessary for quoting results in the usual kilograms per hectare. This is unrealistic as it implies homogeneity of deposition throughout too great an area. The author suggests grams per square meter as the more reasonable unit for this and comparable measurements where small scale sampling is involved and subsequently scaled up to apply to areas useful primarily to those in agriculture.

Furthermore, perhaps because dustfall rates as well as many related variables depend significantly on micro- and meso-scale (up to 30 miles) meteorology, care should be taken to follow established procedures in sample collecting and data processing as exemplified by the American Society of Testing Materials (ASTM) standards for the maintenance of a dustfall network (18). With these limitations in mind, an examination of figures 61 to 63 follows.

Figures 61 to 63 depict monthly means for the three domains studied. As our main concern is sulfur in precipitation, the discussion will emphasize this aspect of the information gathered with only attention given to the total dustfall which is relevant to an interpretation of the sulfur results. The application of various statistical tests to the data as presented in Figures 61 to 66 allow somewhat more objective conclusions to be reached concerning the significance of any apparent difference in rates of deposition.

On this basis it has been demonstrated that for each region sampled, dustfall and sulfur deposition rates do not vary significantly during those months when activity on the land is high - namely June through September. The term "activity" is meant to encompass both anthropogenic pursuits such as farming and increased vehicular traffic as well as all other aspects of the renaissance of biological life. As winter approaches once again, and the harvest is completed all activity which is sustained by the summer growth suddenly wanes as well. A comparable significant decrease in dustfall sulfur accompanies this onset of dormancy.

If the majority of the sulfur found were ascribable to the gas plants, such a dramatic decrease would be unexpected; in fact at a given location

no decrease would be anticipated at all. Furthermore, if one assumes gas plant sulfur emissions to come to earth according to a simple advection-diffusion model such as that used by Benjamin (7), then an exponential deposition pattern such as is shown in Figure 67 would be indicated. Reference to Figures 64 and 65, in which monthly deposition rates for July through October are presented as a function of distance, do not support such an overall trend, although Figure 65 definitely does show a lower rate of sulfur fallout for the Cereal domain during July, August, and September. But this is thought to reflect a lower level of human activity, lower population density, and the change from crop-raising in the Rimbey and Drumheller areas to cattle-grazing as the main agricultural pursuit.

Conventional soil sulfur analyses relate to averages of 6-in cores taken from agricultural soils (19), whereas the sulfur content of fine surface silts is probably much more relevant to an understanding of sulfur in dustfall. Although agricultural soils contain 10 to 100 ppm S, E. Wallick (20) refers to the prevalence of soils in the saline areas of the present study area with as much as 6000 ppm S (0.6 percent). Such material results from the surface evaporation of saline groundwater. The sulfates thus deposited effloresce (lose their water of hydration) to leave a very fine material of higher mobility than bulk soil. In this way windblown particulate could show higher sulfur content than a 6-in core of agricultural soil. Moreover, such a fine material is usually to be found under circumstances where the wind "fetch" is greater than would be expected in the case of agricultural soils, that is at the margins of sloughs or where entire sloughs have dried up. The point established is that the percentages of S reported in Table 16 lie within the range of those percentages found in various terrestrial environments encountered in each of the test zones. X-ray analyses help to substantiate such an explanation of sulfur values in dustfall higher than those established for agricultural soils, because these analyses reveal a high amount of surficial silt-like materials in the dustfall collected.

Table 16 Percentages of $\text{SO}_4\text{-S}$ in Dustfall for the Months June to November, 1975

Month	Location		
	Rimbey	Drumheller	Cereal
June	5.7	---	---
July	1.9	2.5	2.6
August	3.8	2.3	1.5
September	5.7	1.4	1.6
October	1.5	1.6	1.5
November	---	0.54	0.25

2.9.4 Conclusions

1. It is plainly unreasonable to suggest that measurements of sulfur in dustfall at distances greater than 10 km may be confidently related to sour waste gases, as the amounts of unrelated sulfur form the overwhelming majority of the sulfur collected.

2. The amount of sulfur from inorganic natural sources actually deposited in the areas studied probably does not exceed the values found in all three domains for the fall months (October, November), i.e. 0.1 kg/hectare/30 days. This value is assumed to be the absolute upper limit to sulfur originating from gas plants and deposited as dry fallout within the areas studied.

3. $\text{S}^{34}/\text{S}^{32}$ ratios ($\delta^{34}\text{S}$) as obtained from our precipitation (dustfall, rain, snow) gauging stations give no additional information as to what fraction of total sulfur is derived from chimney plumes. This conclusion was reached in consultation with Dr. R. Krouse, University of Calgary. Nevertheless, these data are tabulated in Table 17, and presented graphically in Figure 68 in the interest of future improved interpretive techniques.

4. Analysis of diurnal wind patterns for the areas in question reaffirms the controlling influence of the counter-acting northwest-southeast low level (~ 1500 m) local winds west of the 5th Meridian, and paralleling the Rocky Mountains from Calgary to Rimbey. The existence of such a far-ranging wind system would tend to trap chimney plumes within such a circula-

tion corridor, thereby increasing their residence time within an area west of the 5th Meridian. Examination of similar information would indicate that this system has weakened considerably 50 mi east of the 5th Meridian (Figures 31 to 36). Thus we would again expect a very minimal fraction of gas plant emissions to deposit within the Drumheller and Cereal test areas.

Table 17 S^{34}/S^{32} Ratios ($\delta^{34}S$) From Dustfall, Rain, and Lake
Water in Central Alberta

Sample	$\delta^{34}S$	Type
Drumheller (July 1975)	+ 8.9	Dustfall
Rimbey (July, 1975)	+ 8.9	Dustfall
Rimbey west (July, 1974)	+15.9	Rain
Lacombe (Summer, 1974)	+20.9	Rain
Red Deer South (July, 1974)	+12.1	Rain
Red Deer West (July, 1974)	+15.9	Rain
Gooseberry Lake (July, 1975)	+12.0	Lake water
Vegreville (July, 1974)	+ 4.4	Rain
Fort Chipewyan (July, 1974)	+ 9.0	Rain

SUMMARY AND CONCLUSIONS

Although our primary geographical region of concern in regard to sulfur in precipitation was central Alberta, a province-wide survey of precipitation was realized through the cooperation of Federal Atmospheric Environment weather stations throughout Alberta and its environs. In so doing, we were provided the broader perspective in which to assess the data generated in central Alberta.

Samples of rain, fresh snow, total snow pack, and hail have been analyzed principally for their $\text{SO}_4\text{-S}$ content. The acidity (pH) and specific conductance of representative samples from each of these types of precipitation have been measured in the belief that these factors are related to $\text{SO}_4\text{-S}$ content. Three years of rain frequency and intensity records for central Alberta have also been compiled to assess and the relative contributions of rain-out and dry deposition as mechanisms which bring atmospheric sulfur compounds to earth. From an analysis of these somewhat limited kinds of data, obtained over the three year period 1973-1975, we put forward the following conclusions:

- 1) In previous years, $\text{SO}_4\text{-S}$ values characteristic of a particular location were given as the average of a seasons' sampling. This average value was then used in calculations of rainout efficiency or $\text{SO}_4\text{-S}$ deposition. Primarily because frequency distribution graphs generated in this study are strongly skewed toward low $\text{SO}_4\text{-S}$ values, the median rather than the average is taken to be more representative of a large number of $\text{SO}_4\text{-S}$ results at a given location. Examination of similar data generated by our predecessors also supports this contention. While the point may appear trivial, this change in emphasis in fact pertains to all forms of precipitation collected and its effect is to reduce by 30-40 percent all calculations using concentrations of sulfur in precipitation as a primary input. It tends to reduce by this factor the level at which we may consider sulfur emissions to be of environmental harm or concern to Albertans. This conclusion is far from trivial.
- 2) Rain falling in remote unpopulated areas of Alberta is characterized by very low $\text{SO}_4\text{-S}$ content (0.2 ppm). This amount approximates that found in fresh snow and appears to represent the world-wide background level of $\text{SO}_4\text{-S}$ due to natural sources.

- 3) Amounts of $\text{SO}_4\text{-S}$ in rain and hail greater than 1.0 ppm, previously held to be symptomatic of contamination by industrially generated SO_2 , have been found in rain falling noticeably beyond the influence of such sources. Conversely, some sampling stations in close proximity to sour gas facilities consistently report rain and hail of extremely low $\text{SO}_4\text{-S}$. Therefore, high $\text{SO}_4\text{-S}$ content by itself cannot unconditionally be the result of high industrial SO_2 emissions.
- 4) Analyses of rain frequency data for central Alberta strongly suggests that, in that part of the province, rainout and dry deposition of $\text{SO}_4\text{-S}$ are of equal importance. Comparison of $\text{SO}_4\text{-S}$ in rain and fresh snow with that of total depth of snow and dustfall independently support this contention.
- 5) Given that agricultural land requires about 10 lbs of sulfur per acre during the growing season, only 2 lbs of this can be contributed throughout the year by sources other than direct and planned application by man.
- 6) Using average seasonal data for sulfur in rain and hail along with monthly plant SO_2 emissions to calculate rainout and washout efficiencies [such as those derived by Hitchon and Summers (1)] may afford reasonable numbers; however, such calculations can only have meaning when applied to a single precipitation event and it must define the source(s) of sulfur input to the storm in question. Analysis of low level diurnal winds prior and during convective storms also intimate SO_2 emissions from a given plant ought to come to earth in rain to the northwest of that plant rather than be deposited isotropically about the plant. Only a comprehensive assault upon single precipitation events will advance our knowledge of sulfur source and budget from sour gas plants.
- 7) The above statements gain added support from the following conclusion derived from the geographical distribution of $\text{SO}_4\text{-S}$ values obtained during individual summer rains. The range of $\text{SO}_4\text{-S}$ values found in rain from a given storm is generally small (0-2.0 ppm $\text{SO}_4\text{-S}$). This result is independent of the extent of the storm in question and hence independent of the number and

size of sour gas plants under the storm. From this one can conclude either that rainout efficiency varies from storm to storm or that emissions from all sulfur plants in central Alberta contribute to a uniform pool of SO_2 over central Alberta. Both of these conclusions are speculative and should be amenable to verification.

- 8) Consideration of low level winds in central Alberta reveals a daily southeast-northwest circulation pattern about 1500 m deep which is capable of increasing the residence time of any chimney plumes in the energy corridor trapped under this ceiling. This system parallels the Rocky Mountains and extends from Calgary to Rimbey. East of Red Deer such diurnal behavior has moderated to the point where only SO_2 emissions attaining heights greater than 1500 m will subsequently be available for future deposition to ground, because such emissions will have then become part of the upper level westerly air flow. It is surmised that, perhaps because this oscillating air flow creates a uniform SO_2 concentration over central Alberta, an increase of five to ten times in the SO_2 available to a storm does not affect the median $\text{SO}_4\text{-S}$ for any storm in central Alberta regardless of its physical size (see 7 above).
- 9) On the whole, the pH of Alberta rain is still typical of non-industrial environments throughout the northern hemisphere. It is thus in contrast to the low pH (less than 5.5) rains observed in the industrial areas of eastern Canada, the U.S. and Europe.
- 10) Much of Alberta's snow originates in Arctic air masses which pass over areas devoid of any industrial activity. Clean snow-producing air masses therefore pass from the west-northwest through Alberta under relatively stable meteorological conditions with little vertical transport of air. Under these conditions, SO_2 would be trapped in the lowest few thousand feet of the atmosphere with little chance to participate in the precipitation mechanism. These facts account for the uniformly low values for $\text{SO}_4\text{-S}$ (0.1-0.2 ppm) in fresh snow.
- 11) Possibly because of the lower particulate content of the atmosphere in winter, occurrences of acidic snow (pH less than 5.5)

have been encountered. In these cases, pH calculated from the $\text{SO}_4\text{-S}$ content of the snow agrees with the measured pH and suggests that sulfuric acid is the major contaminant. In all other cases where pH, $\text{SO}_4\text{-S}$ and specific conductivity have been determined on a sample, no apparent connection can be established among these variables. A more complete chemical description of precipitation samples is indicated.

- 12) Environmental chamber studies show that up to 1.2 lbs of $\text{SO}_4\text{-S}$ can be absorbed by test soils when exposed to an atmosphere containing a constant 25 ppb SO_2 . Under these conditions, the same soils exhibited a 0.1 unit drop in pH. While signifying that appreciable quantities of sulfur can be taken up by soils from air containing even minute amounts of SO_2 , such a result also emphasizes the need for comparable field data, especially in regard to the SO_2 gradient at the soil-atmosphere interface.

Three dustfall survey regions in central Alberta, each having a density of one station per three square miles, were operated in 1975 to statistically evaluate the amount of sulfur deposited through this pathway and to ascertain whether the sulfur found could be related back to SO_2 emissions from gas plants. Analyses for twenty-two elements were also performed on these dustfall samples. The following results arising from this survey are to be stressed.

- 1) It is unjustifiable at the present time to suggest that quantities of sulfur in dustfall at distances greater than 10 km from an industrial source may be confidently related to sour waste gas, as the amounts of unrelated sulfur form the overwhelming majority of the sulfur collected.
- 2) The amount of sulfur from inorganic natural sources deposited in the regions of central Alberta studied probably does not exceed the quantity found in all three domains for the months October and November; that is, 0.1 kg per hectare per thirty days. This value is taken to be the upper limit to sulfur originating from gas plants and deposited in dry fallout within the areas studied.

4. RECOMMENDATIONS

- 1) A variety of analytical procedures for the determination of $\text{SO}_4\text{-S}$ are currently in use in the province. Oddly enough the two methods most highly recommended by the U.S. Environmental Protection Agency have received little attention here. The same multiplicity of analytical methods certainly applies to the measurement of many other species of environmental concern. Some attempt should be made, perhaps starting with $\text{SO}_4\text{-S}$, to establish a standard sample exchange to intercompare on a regular basis the reliability of the various analytical procedures in use. In this context the need for a facility capable of generating and maintaining known ppb concentrations of suspected gaseous pollutants has also been recognized. The value of such equipment in the standardization of commercial pollution monitors is widely recognized.
- 2) Because there has been no apparent change in the amount of $\text{SO}_4\text{-S}$ in any of the removal pathways monitored over the past seven years even though pollutant emission restrictions have become more stringent over that period, it becomes increasingly necessary for us to search all past data sources to either confirm or deny this assertion. We are also compelled to maintain the present program of monitoring $\text{SO}_4\text{-S}$ in precipitation in the future so that our emission standards reflect real situations and possibilities in Alberta rather than simply responding to legislation promulgated in other densely populated areas of the world.
- 3) Many of the recommendations arising out of this report can best be carried out through intensive study of single storm events. In this category we could place the measurement of rain pH, $\text{SO}_4\text{-S}$ content as a function of time period sampled during the storm, geographical location and so on. These require large manpower and equipment inputs and are therefore anticipated to be very expensive. Such studies have already been done in locations where the pollution problems were more acute than here. It is problematic whether the peculiarities of the Alberta environment are sufficient justification to repeat the exercise. We simply do not have the urgency factor which exists, for example, in the St. Louis airshed, the eastern U.S. or northern Europe. In many cases we are repeating measurements already

done in other parts of the world, while having only a small fraction of the pollutant problem.

- 4) The individuals subjective response to suspected pollutant sources has received almost no attention by granting agencies. We are well aware of the deprivation suffered by Pincher Creek residents in the early days of sour gas processing. We may not be as aware how well entrenched these opinions and attitudes regarding the gas industry still are among central Alberta residents. Social scientists should be prompted to sample this attitude, compare it where possible with fact and proceed to the education step which the local plant operators have apparently neglected, except perhaps for their immediate employees. Even this statement should be amenable to justification by such a much-needed survey.

This could initiate a grass-roots source of research ideas. As an example, many central Alberta residents associate the advent of the sour gas industry with intensified rusting of fence wire and farm machinery. Perhaps it is at this level that we should concentrate our environmental research efforts.

- 5) In a completely different vein and perhaps before advising against commitment of funds to the types of interdisciplinary projects discussed in 3), a serious effort should be made to research the practicality of a Western Canadian Atmospheric Research Center sited in Alberta. We are all aware of inter-related research projects presently being pursued by groups or individuals in virtual isolation or unawareness of each other. Were these meteorologists, chemists and physicists who have a common interest in atmospheric phenomena were grouped together their productivity could obviously be maximised and their common needs pooled for economic benefit. Vital baseline data for many tropospheric species not necessarily considered as pollutants but perhaps relevant to their atmospheric transformations are presently unavailable in this locale. There is no presently existing organization whose mandate includes a responsibility for these kinds of tasks.

The presence of various unique geographical features such as the Rocky mountains, great plains, nearness to severe extremes of climate and the role these factors play in dictating the quality of life in what is anticipated to be a highly industrialized future is added incentive for consideration of such an establishment in Alberta.

- 6) The unreasonably high $\text{SO}_4\text{-S}$ observed in Calgary rain is a consequence of the poor location for the collection of this type of sample. It is suggested that another AES station could profitably be located in the Calgary area, and that this facility not be adjacent to the major runways of an international airport. Similarly, the high median values obtained from the Edson AES station - values indicative of the Whitecourt gas complex - would seem to temper the choice of Edson as a meteorological outpost contributing baseline data to a world-wide network.
- 7) We have revealed the presence of a unique summer wind pattern in central Alberta which could act to smooth out expected pollutant concentration gradients, thus providing a single uniform source of SO_2 upon which convective storms could act. A catalogue of summer and winter atmospheric SO_2 concentrations over central Alberta should be attempted in order to ascertain whether this wind pattern in fact produces such a pool of SO_2 over the energy corridor. In the absence of the ground absorption mechanism, as would be expected in winter, this concentration of SO_2 should be enhanced, as more stable atmospheric conditions would be expected in winter.
- 8) Because no relationship has been found between sample pH, specific conductance and $\text{SO}_4\text{-S}$, a more complete chemical analysis of precipitation is desirable in order to pinpoint those species which control the acidity of precipitation.
- 9) We have observed that the pH of snow can be less than that of rain and hail. The tentative reason given relates to the lower atmospheric concentration of neutralizing ions prevailing during winter. A program should be considered whose object would be to wind directionally sample the particulate content of the lower atmosphere over a period of one year, preferably in proximity to a sour gas facility, with a view toward testing the above hypothesis.
- 10) We have shown the pH of Alberta rain to be typical of a non-industrial environment (pH greater than 5.5). Additionally, the near equivalence of dry fallout and rainout as $\text{SO}_4\text{-S}$ deposition mechanisms has been stressed. Further research bearing on these topics is warranted on these matters by the seemingly conflicting conclusions reached by Nyborg et. al., (4) as a result of experiments dealing with sulfur uptake by test soils.

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6. FIGURES AND TABLES

Table (2)

ANALYSIS OF RAIN & SNOW FROM WEATHER STATIONS. SPRING AND SUMMER 1974

ATHABASCA	BANFF	CALGARY	COLD LAKE	CORONATION	EDMONTON	EDSON	FAIRVIEW	Ft. McMURRAY	Ft. St. JOHN B.C.
April 12 0.2									
May 24 1.0					May 23 2.2				May 26 0.6
June 8 0.4	June 7 0.4 June 26 0.6	June 7 12.2		June 3 0.4 June 4 1.0 June 6 0.3 June 8 1.5	June 3 0.3 June 4 1.7	June 6 1.0		June 6 0.6 June 28 1.0	June 26 0.7
July 3 0.8 July 5 0.1 July 9 0.1 July 9 0.4 July 11 0.4* July 12 0.3		July 1 11.9	July 24 0.2 July 30 0.3	July 30 0.6		July 8 0.9	July 30 0.3	July 9 0.3 July 25 1.5	July 10 0.2
Aug. 23 0.8	Aug. 11 0.1 Aug. 13 1.1	Aug. 10 0.9 Aug. 19 11.8	Aug. 6 0.3 Aug. 16 0.3	Aug. 10 0.9		Aug. 7 1.7 Aug. 11 0.2 Aug. 19 0.1	Aug. 18 0.1 Aug. 20 1.4 Aug. 23 0.3	Aug. 18 0.2 Aug. 23 0.2	Aug. 7 0.3 Aug. 18 0.1
*Hail	Sept. 4 1.3 Sept. 7 0.5 Sept. 10 0.2		Sept. 6 0.1 Sept. 10 0.2			Sept. 5 0.6 Sept. 9 0.8	Sept. 4 0.3 Sept. 9 0.2		
	Oct. 11 1.1					Oct. 2 1.3 Oct. 6 0.7			
Ft. SMITH N.W.T.	GRANDE PRAIRIE	JASPER	LACOMBE	MEDICINE HAT	PINCHER CREEK	PEACE RIVER	ROCKY MOUNTAIN HOUSE	SLAVE LAKE	VEGREVILLE
May 27 0.3	May 23 0.9	May 23 2.3 May 27 0.6	May 23 2.3	May 31 1.5	May 29 0.6 May 30 0.4				May 24 5.0
June 11 1.6 June 13 0.1 June 19 0.1		June 6 0.8 June 22 0.7 June 27 0.1 June 30 0.3	June 4 3.2 June 6 1.9	June 24 8.0 June 26 0.6		June 27 0.3			June 4 2.0 June 4 1.0 June 8 1.1 June 26 3.4
July 2 0.3 July 7 0.3 July 12 1.2 July 16 0.1 July 26 0.2	July 3 3.0 July 30 1.4	July 5	July 5 1.7 July 5 0.4 4.7 July 22 5.0	July 8 1.1 July 30 9.7		July 1 0.1 July 2 0.2	July 8 0.9	July 11 0.0 July 11 0.4 July 30 0.2	July 30 2.2
Aug. 8 0.4 Aug. 21 0.6	Aug. 8 0.1 Aug. 18 0.1 Aug. 18 0.1	Aug. 10 8.5 Aug. 12 1.9 Aug. 18 0.4 Aug. 23 0.2	Aug. 6 2.5 Aug. 29 1.1	Aug. 8 1.1 Aug. 13 0.1	Aug. 8 0.6 Aug. 10 1.1 Aug. 12 0.1 Aug. 29 4.0 Aug. 31 0.8	Aug. 20 0.2 Aug. 23 0.3 Aug. 27 0.3	Aug. 9 0.3 Aug. 11 0.1 Aug. 18 0.2 Aug. 22 1.1		Aug. 7 2.4 Aug. 14 2.8 Aug. 17 1.9
Sept. 19 0.3	Sept. 4 0.3				Sept. 10 1.7	Sept. 27 0.1	Sept. 27 1.2 Sept. 29 0.4	Sept. 5 0.1 Sept. 6 0.2 Sept. 9 0.2	Sept. 9 0.4 Sept. 10 0.4

ANALYSIS OF RAIN & SNOW FROM WEATHER STATIONS. SPRING AND SUMMER 1975

ATHABASCA		BANFF		CALGARY		COLD LAKE		CORONATION		EDSON		EDM. INTL A/Pt		FAIRVIEW		FT. CHIPEWYAN	
May 23	0.5			May 24	5.0	May 23	0.3			May 4	0.2	May 4	1.6			May 24	10.2
May 24	0.05			May 29	8.0	May 30	0.2			May 15	1.5	May 23	1.5				
May 25	0.0			(no date)	0.0					May 22	1.3						
										May 23	1.6						
										May 29	1.2						
June 7	0.0	June 24	0.4			June 3	0.6									June 16	1.0
						June 3	0.2	June 19	5.0	June 6	0.0	June 13	0.55				
		July 11	0.8	July 3	11.1	June 14	0.4					June 15	2.6	June 26	0.6		
		July 13	0.05	July 17	6.8	June 27	0.2					June 26	0.6	June 27	0.2		
		July 15	0.05	July 21	6.0												
		July 17	0.05	July 28	15.8							July 6	0.6			July 5	2.0
		July 28	0.05									July 18	0.0			July 14	2.0
		July 31	0.05													July 21	2.0
		Aug. 16	1.20														
		Aug. 16	2.00					Aug. 21	1.0								
		Aug. 22	1.00									Aug. 3	0.05				

Ft. McMURRAY		Ft. St. JOHN		Ft. SMITH		Ft. VERMILLION		GRANDE PRAIRIE		JASPER		LACOMBE		MEDICINE HAT		PEACE RIVER	
Apr. 27	0.05																
May 6	0.4	May 5	0.5	May 8	0.4					May 4	0.8	May 4	0.8	April 30	0.4		
		May 13	0.3	May 14	0.4					May 25	0.2	May 15	1.6				
				(no date)	0.9												
June 8	0.6	June 2	0.4	June 9	0.4	June 3	0.6	June 16	0.2	June 5	0.2	June 16	1.4				
June 28	0.05	June 14	0.2	June 17	0.0	June 7	0.2	June 27	0.5	June 15	0.2			June 18	3.6		
		June 27	0.05	June 25	1.5					June 23	0.2			June 19	0.2	June 27	0.05
										June 27	5.6					July 27	0.6
		July 14	0.1									July 3	0.4				
			0.05														
		Aug. 3						Aug. 22	2.0					Aug. 2	0.1		
								Nov. 4	0.2					Sept. 17	0.4	Sept. 2	0.4
																Sept. 2	0.6
																Sept. 3	0.4

PINCHER CREEK		SLAVE LAKE		VEGREVILLE	
May 18	0.05	May 22	0.2	May 1	1.6
		May 24	0.6	May 15	1.7
June 7	0.6	June 7	0.2	June 2	1.4
June 8	0.3			(no date)	2.0
June 15	0.2				
June 18	0.4	June 26	0.05	June 26	5.2
		July 16	0.0		
		Aug. 1	0.1		

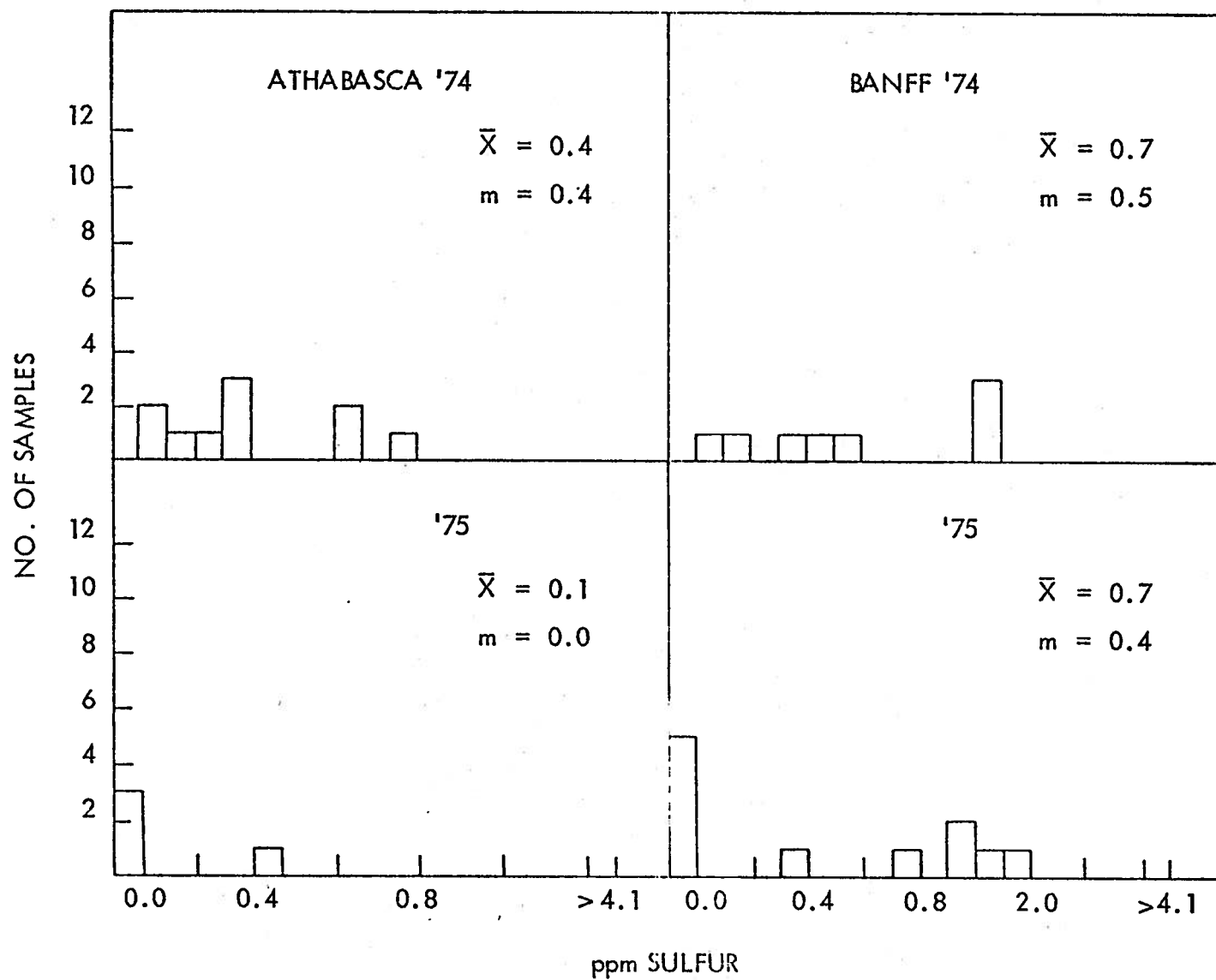


Figure 1: Range of SO₄-S values for all precipitation events at the indicated location. Summer 1974 and 1975 \bar{X} = Average m = Median

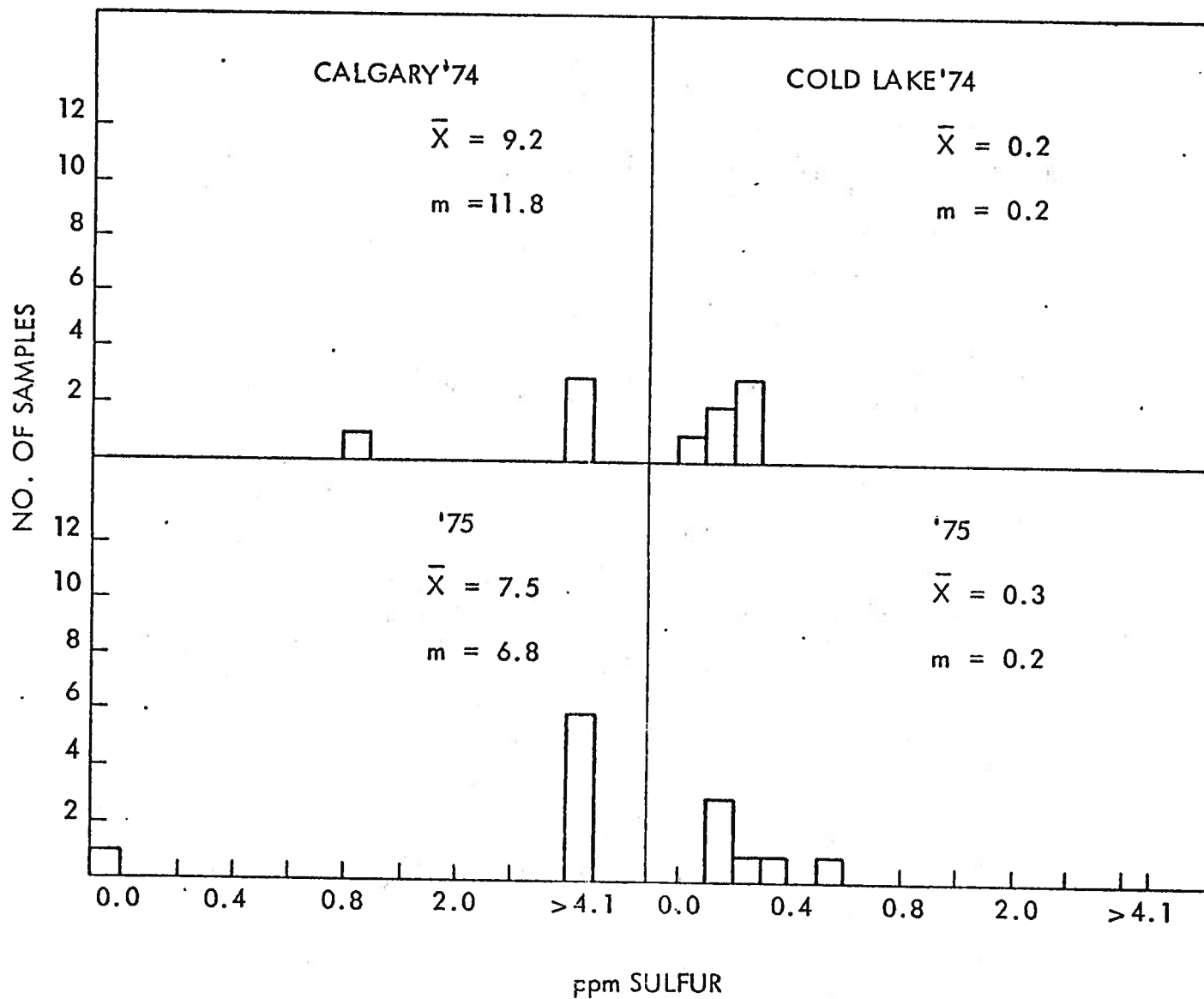


Figure 2: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

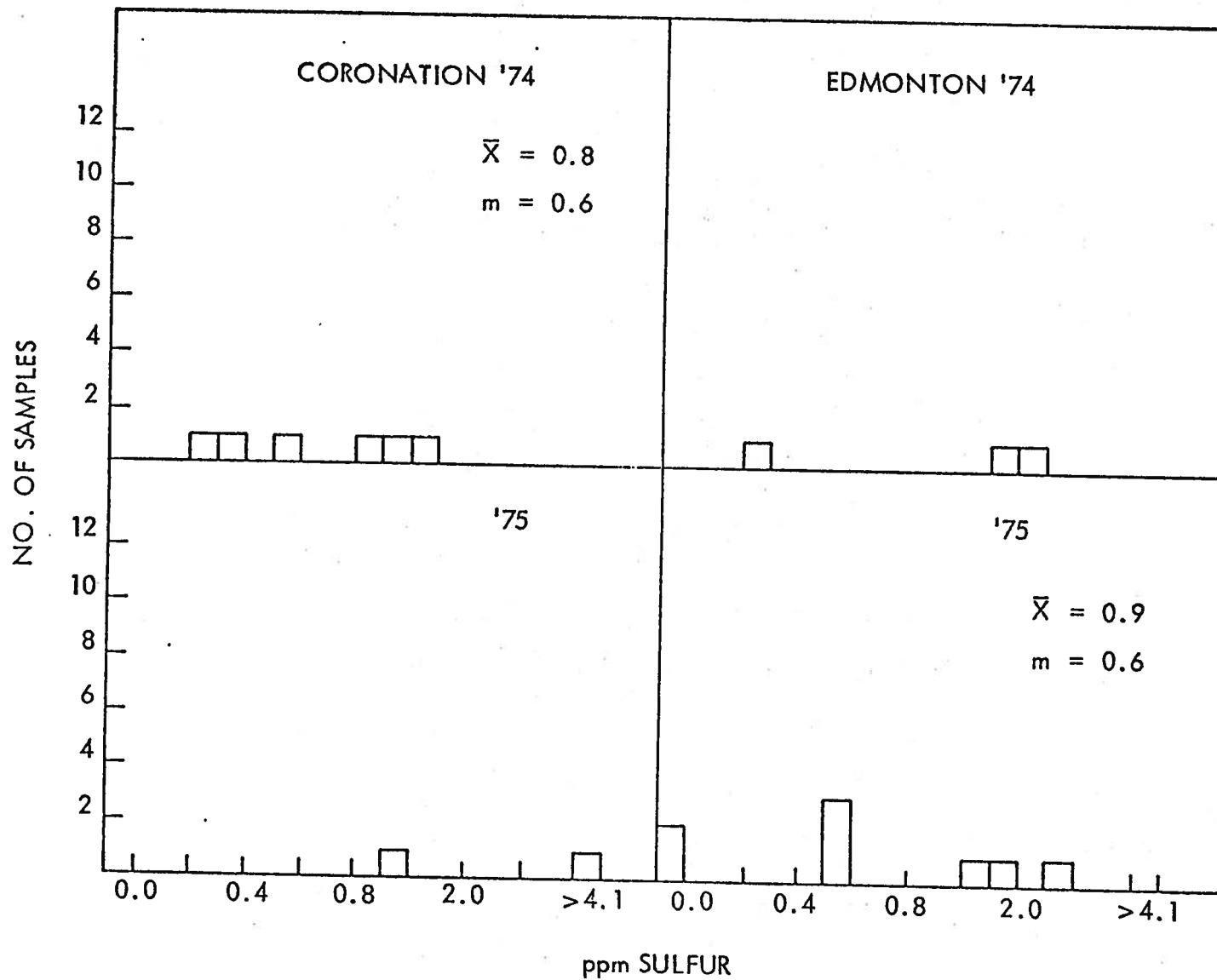


Figure 3: Range of $\text{SO}_4\text{-S}$ values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

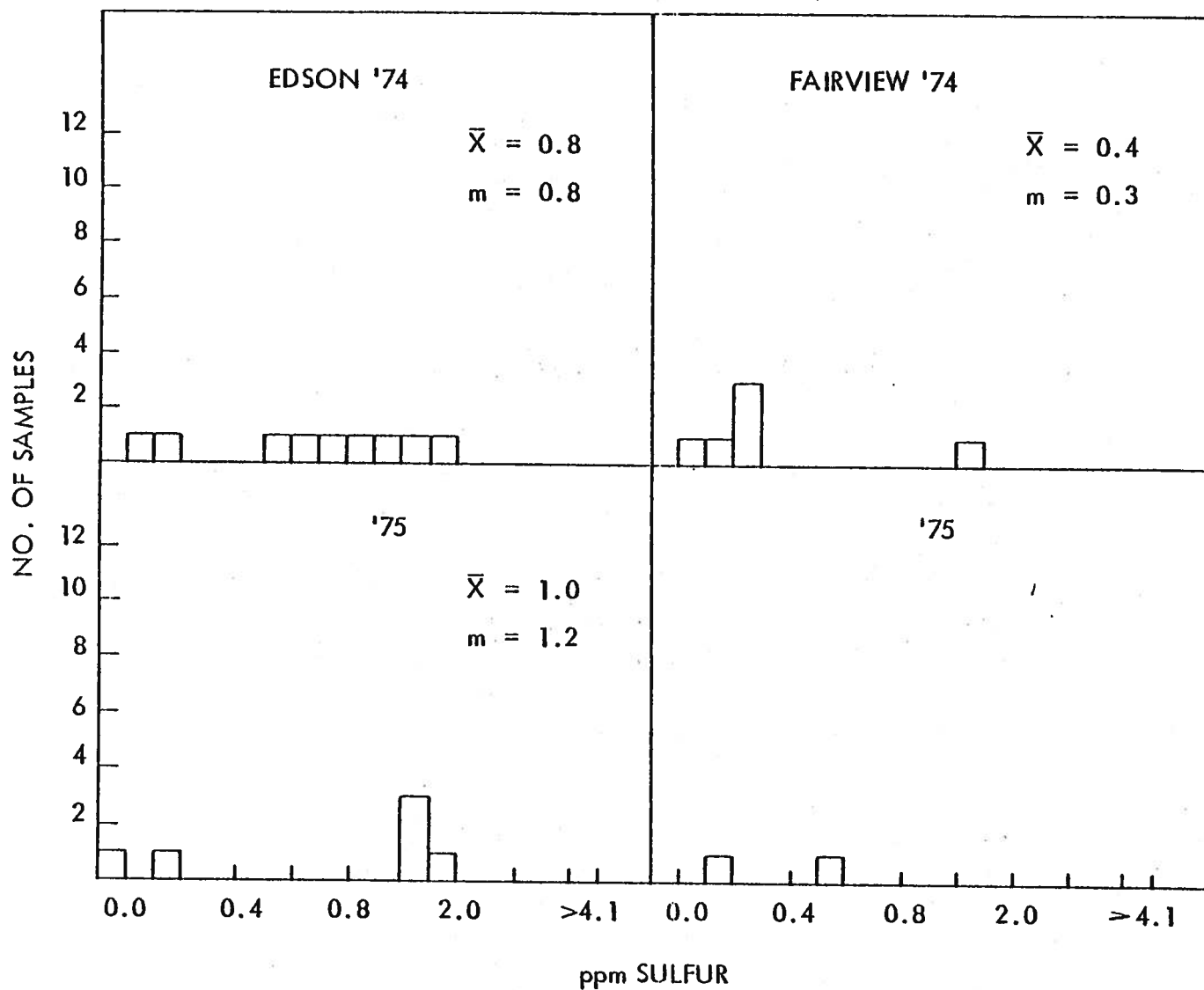


Figure 4: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

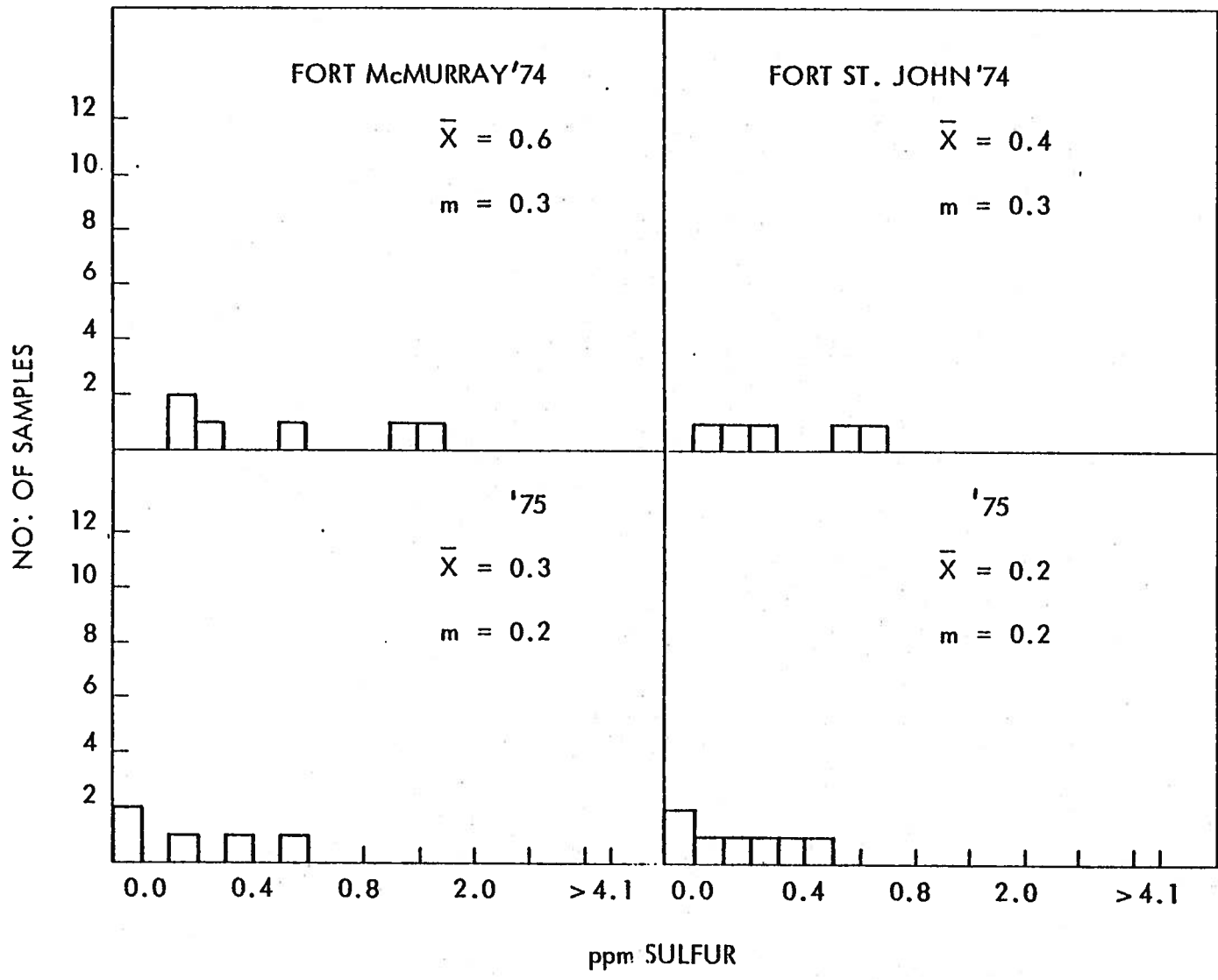


Figure 5: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

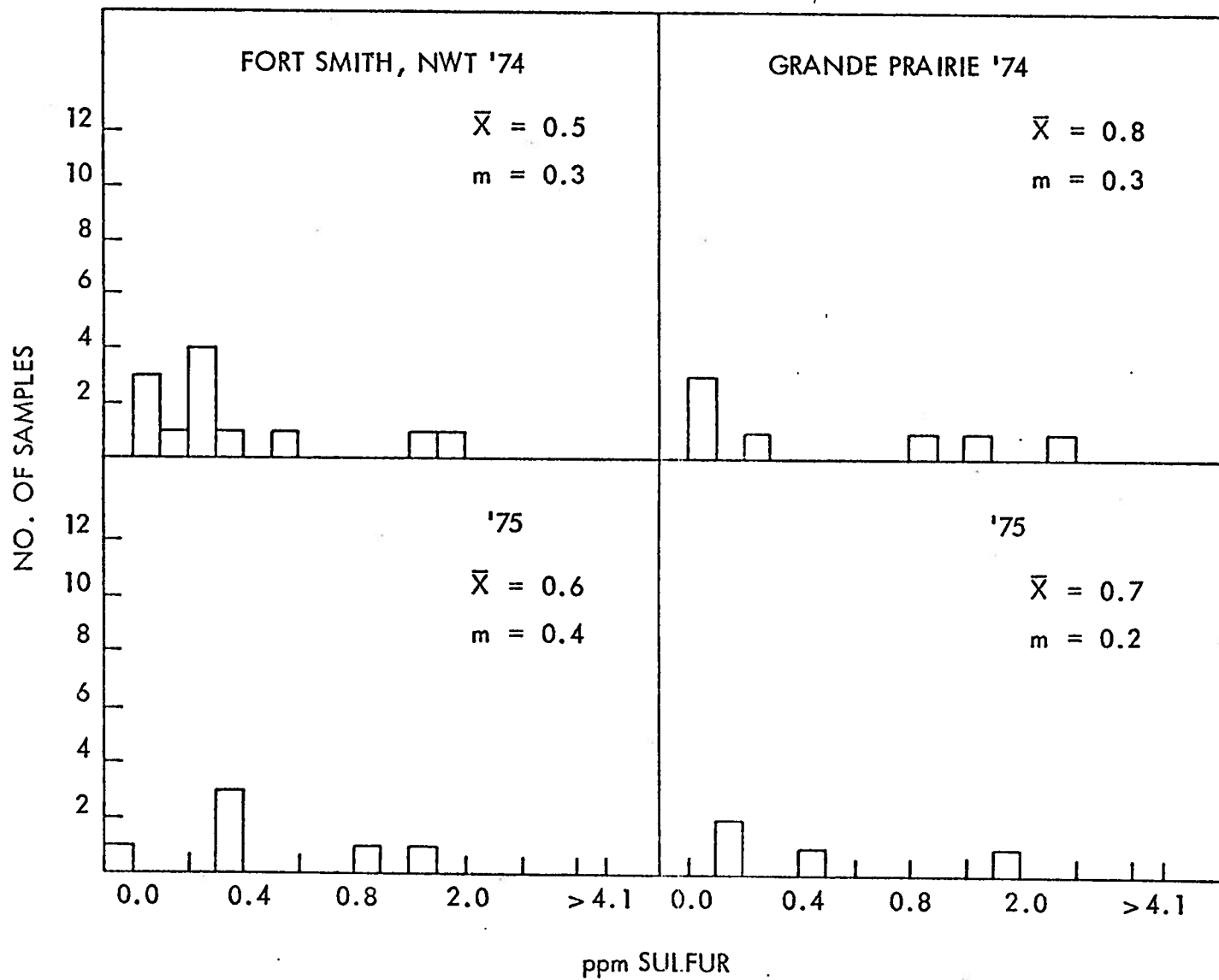


Figure 6: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

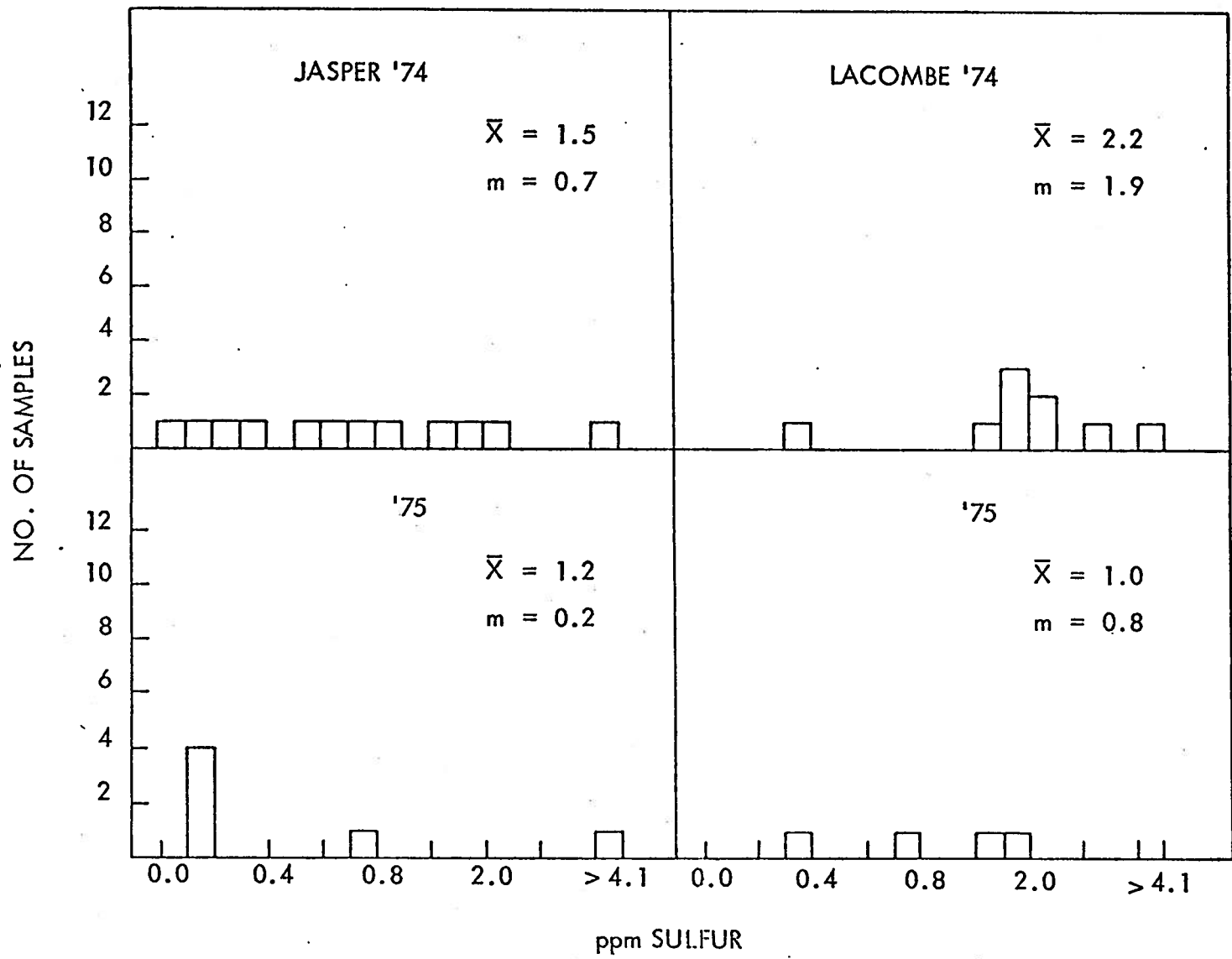


Figure 7: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

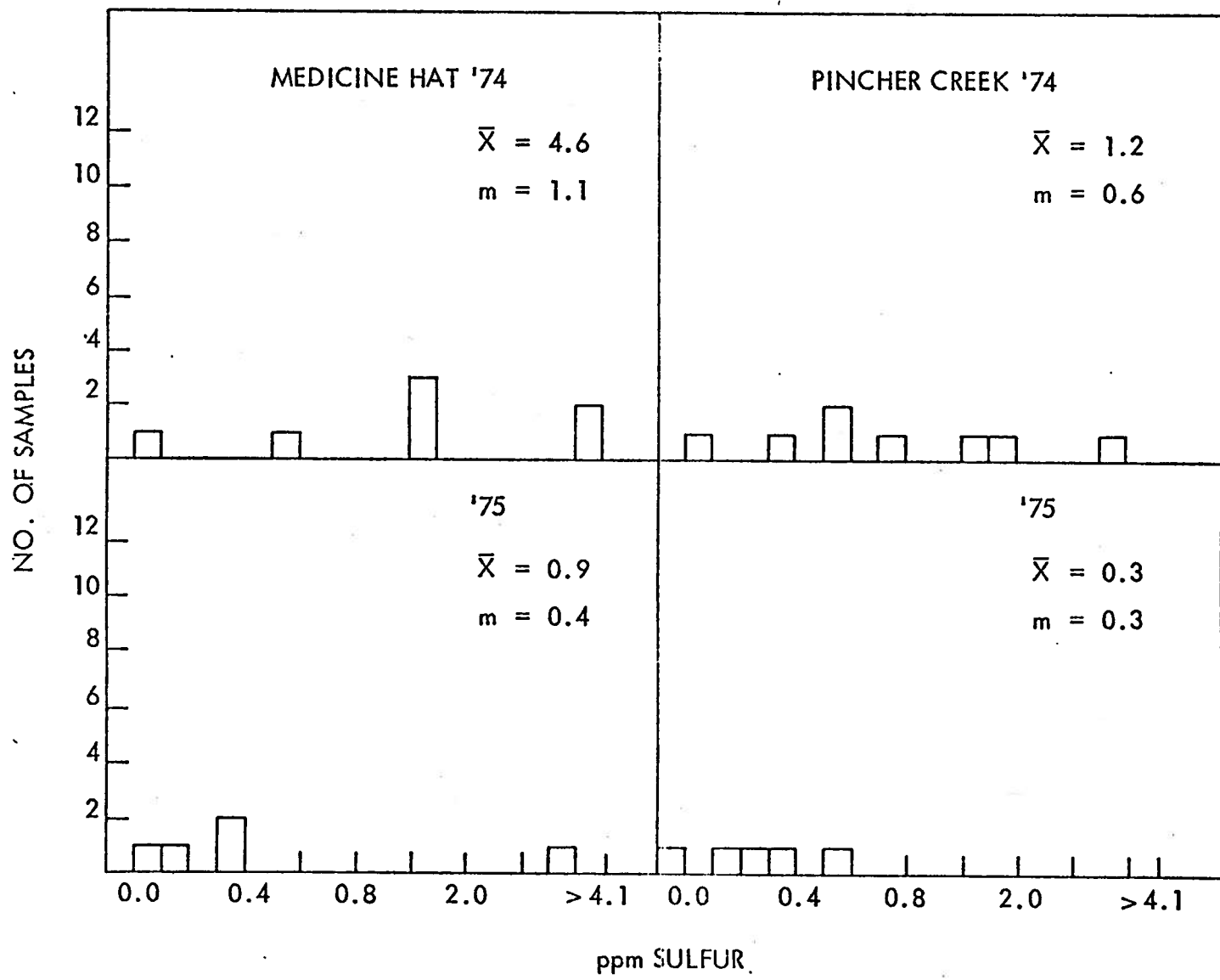


Figure 8: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

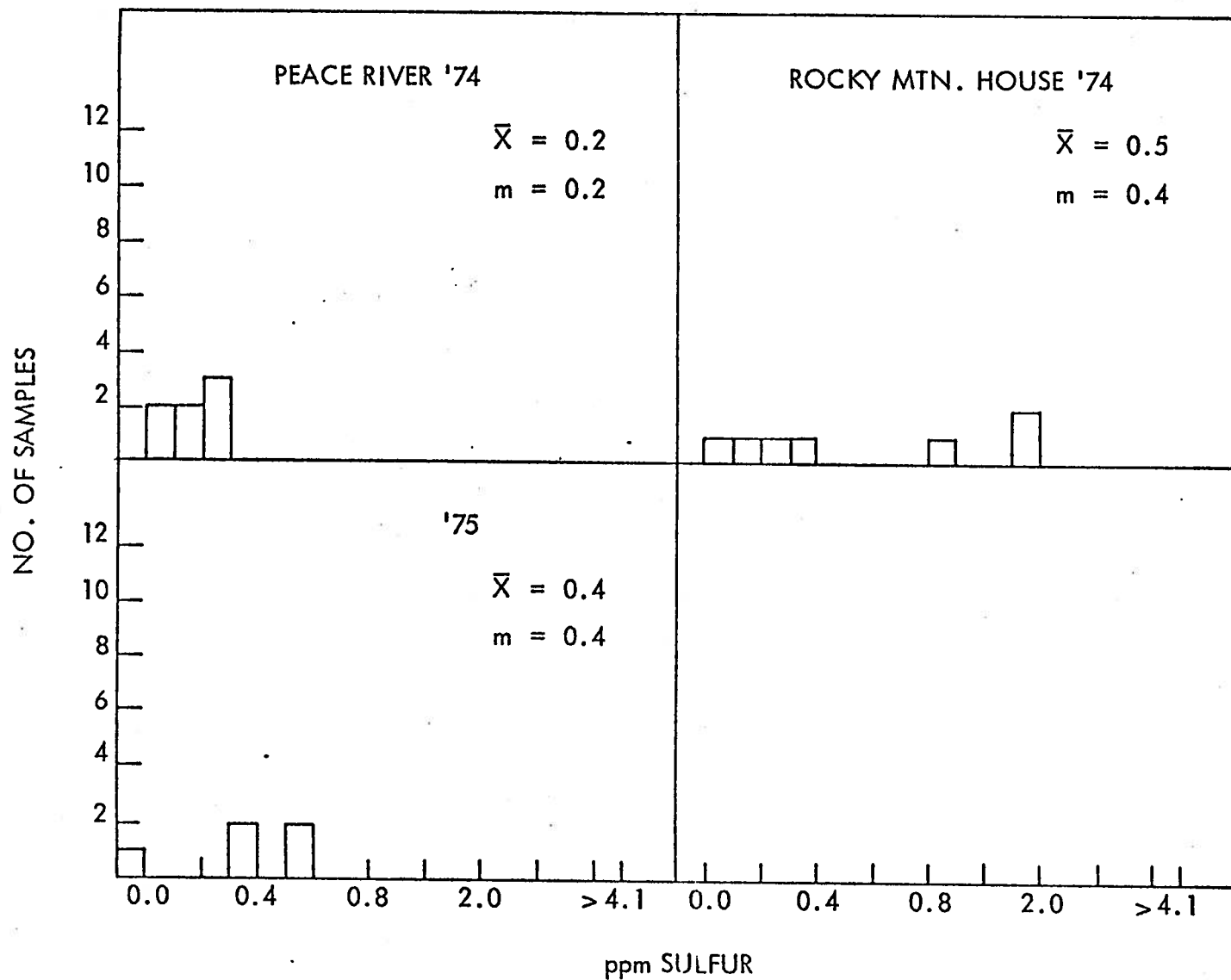


Figure 9: Range of SO_4-S values for all precipitation events at the indicated location: ⁴Summer 1974 and 1975 \bar{X} = Average m = Median

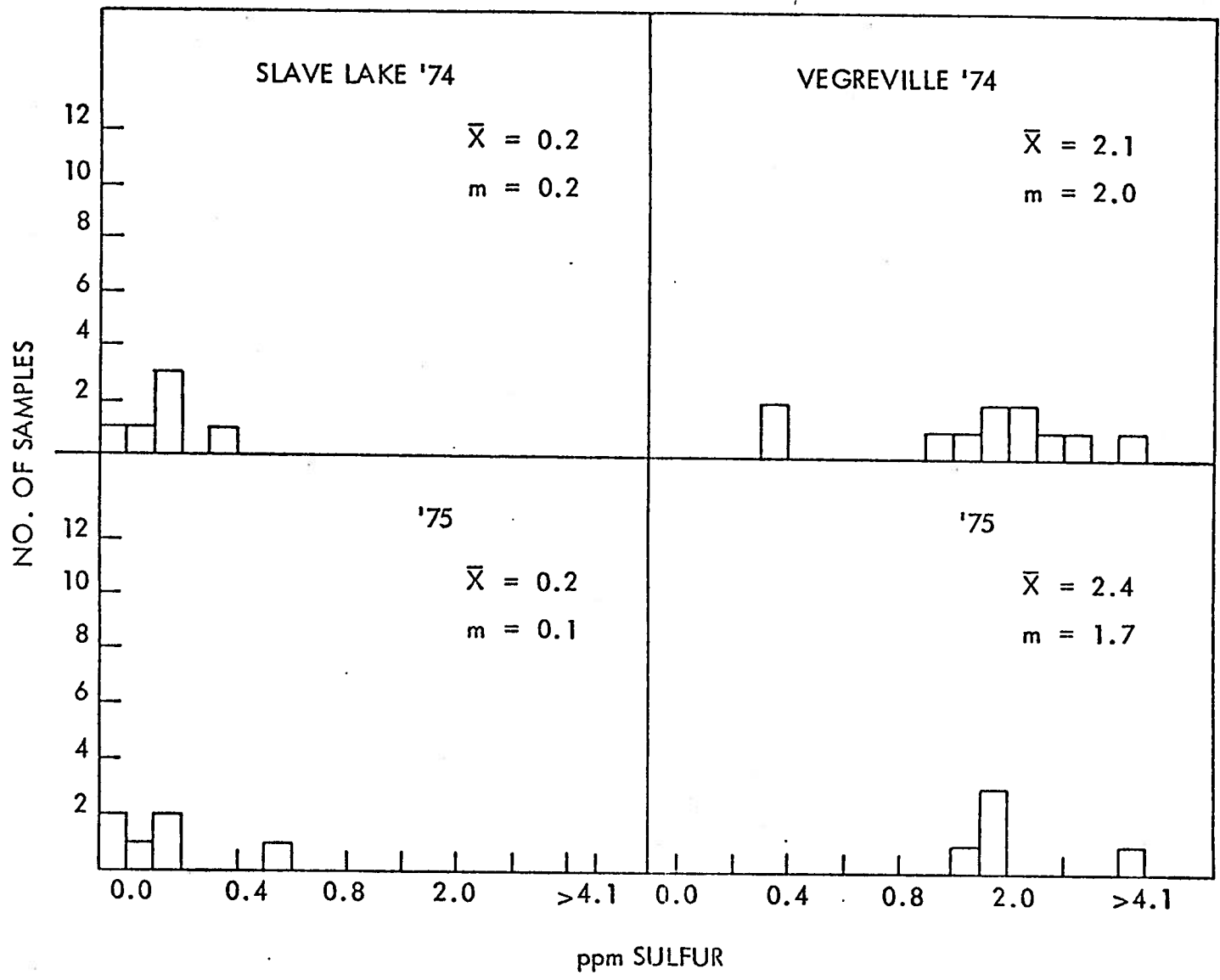


Figure 10: Range of SO_4-S values for all precipitation events at the indicated location: Summer 1974 and 1975 \bar{X} = Average m = Median

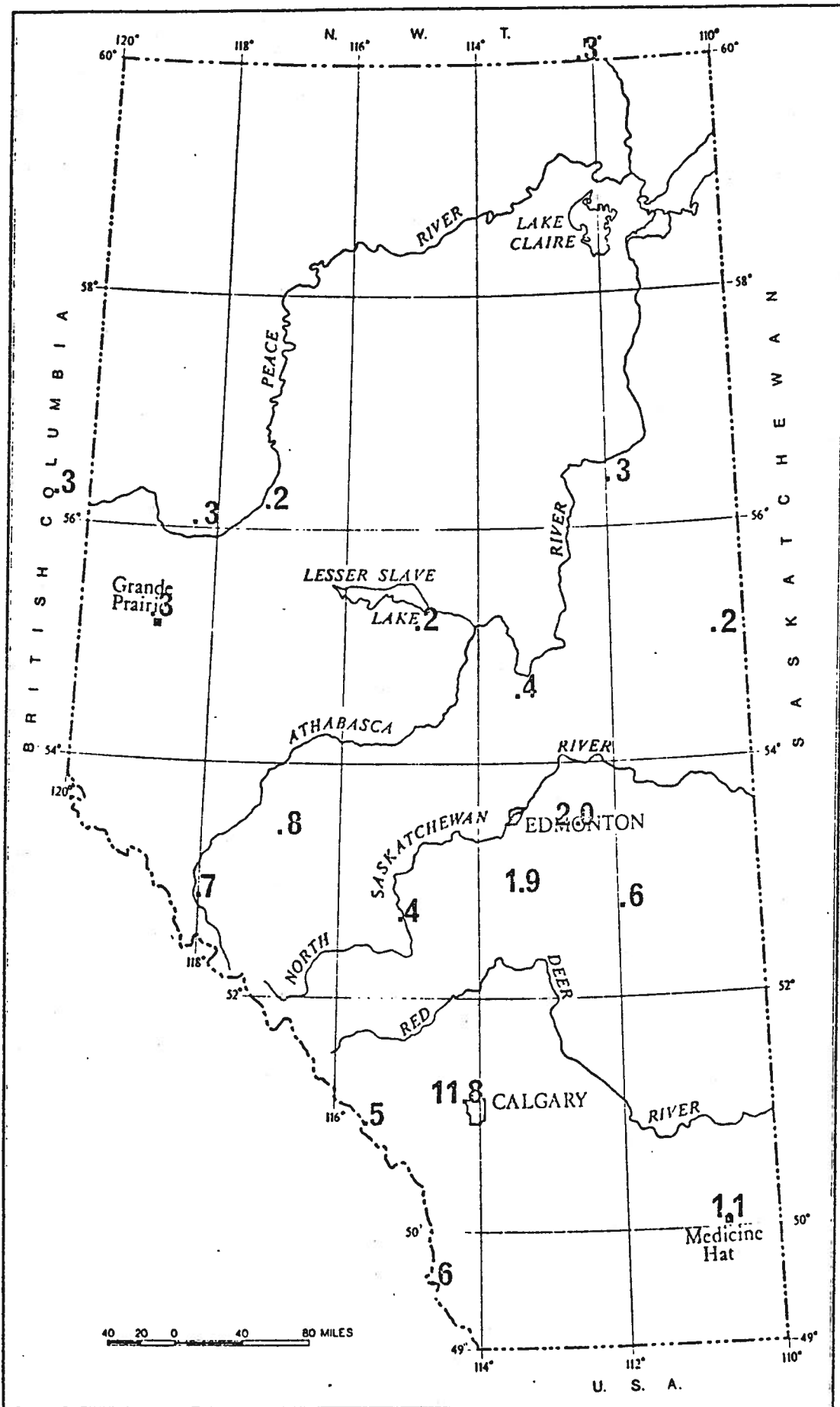


Figure 11: Median SO₄-S (ppm) in rainfall as obtained from AES weather stations, 1974.

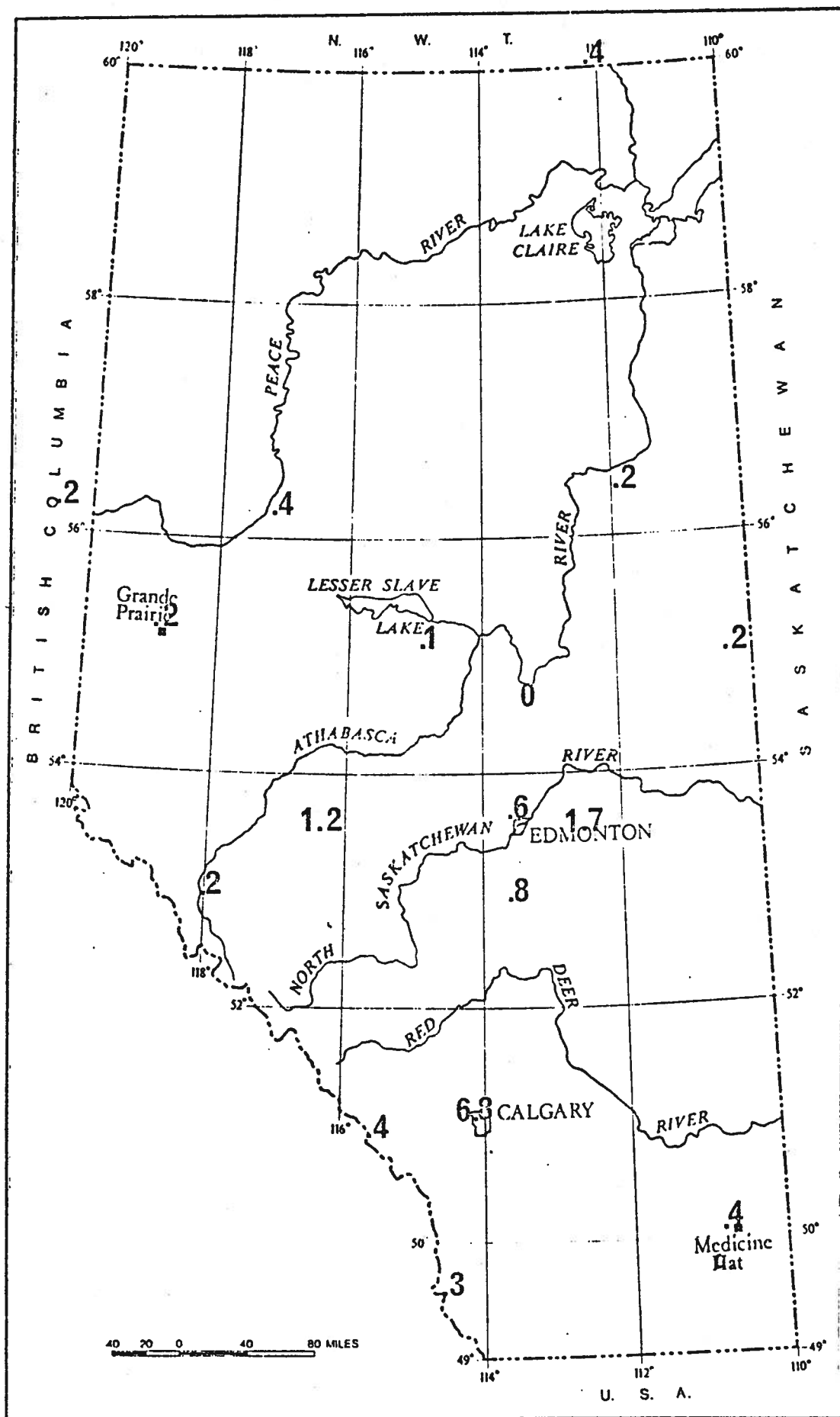


Figure 12: Median SO₄-S (ppm) in rainfall as obtained from AES weather stations, 1975.

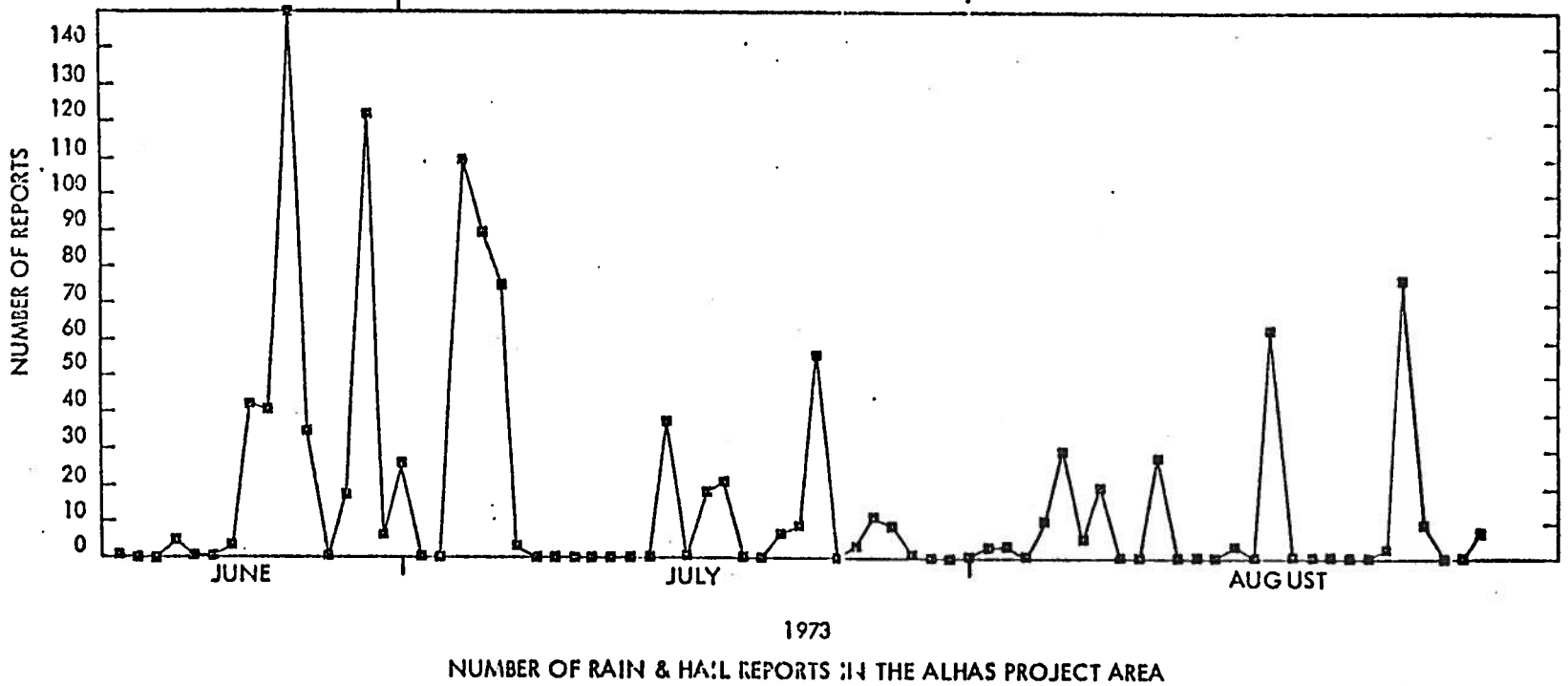


Figure 13: Frequency of rain and hail reports in the ALHAS project area, 1973.

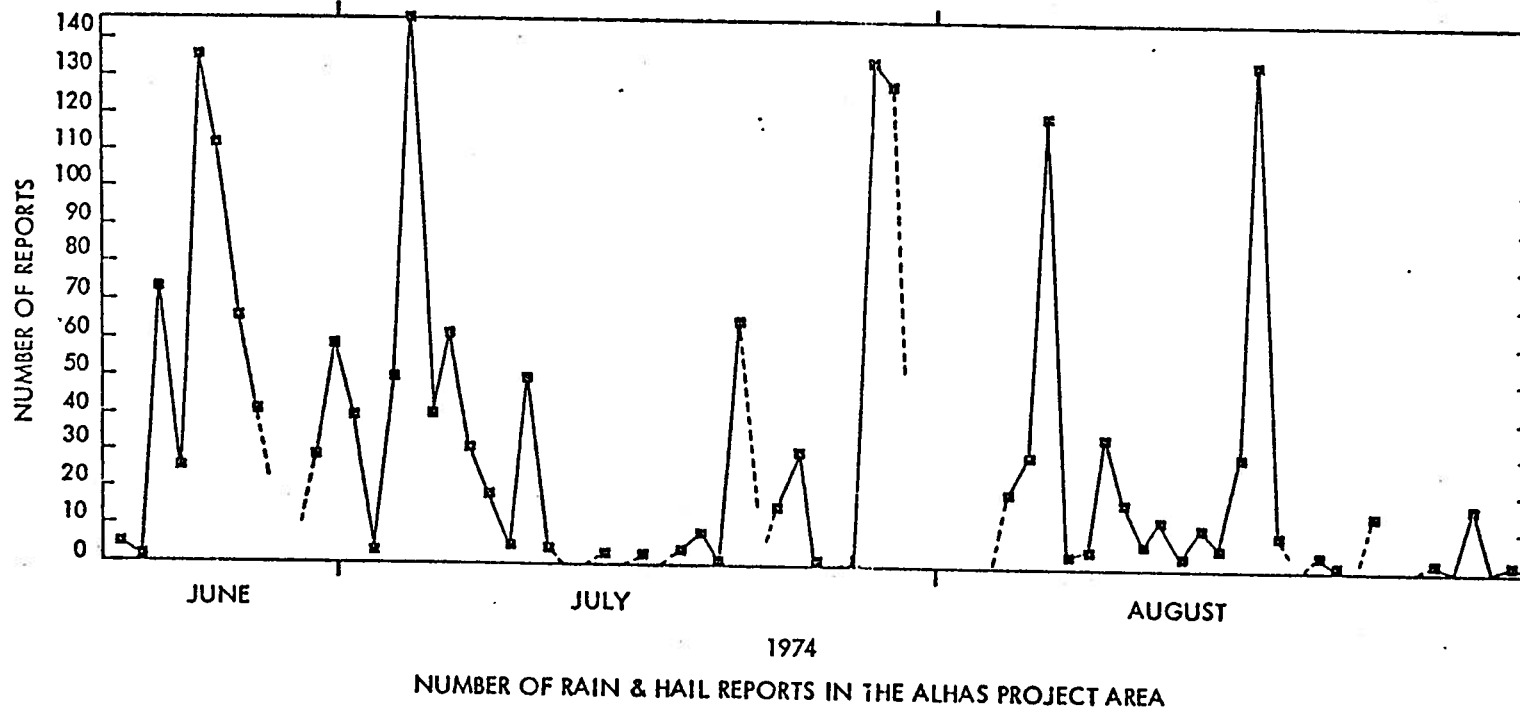


Figure 14: Frequency of rain and hail reports in the ALHAS project area, 1974.

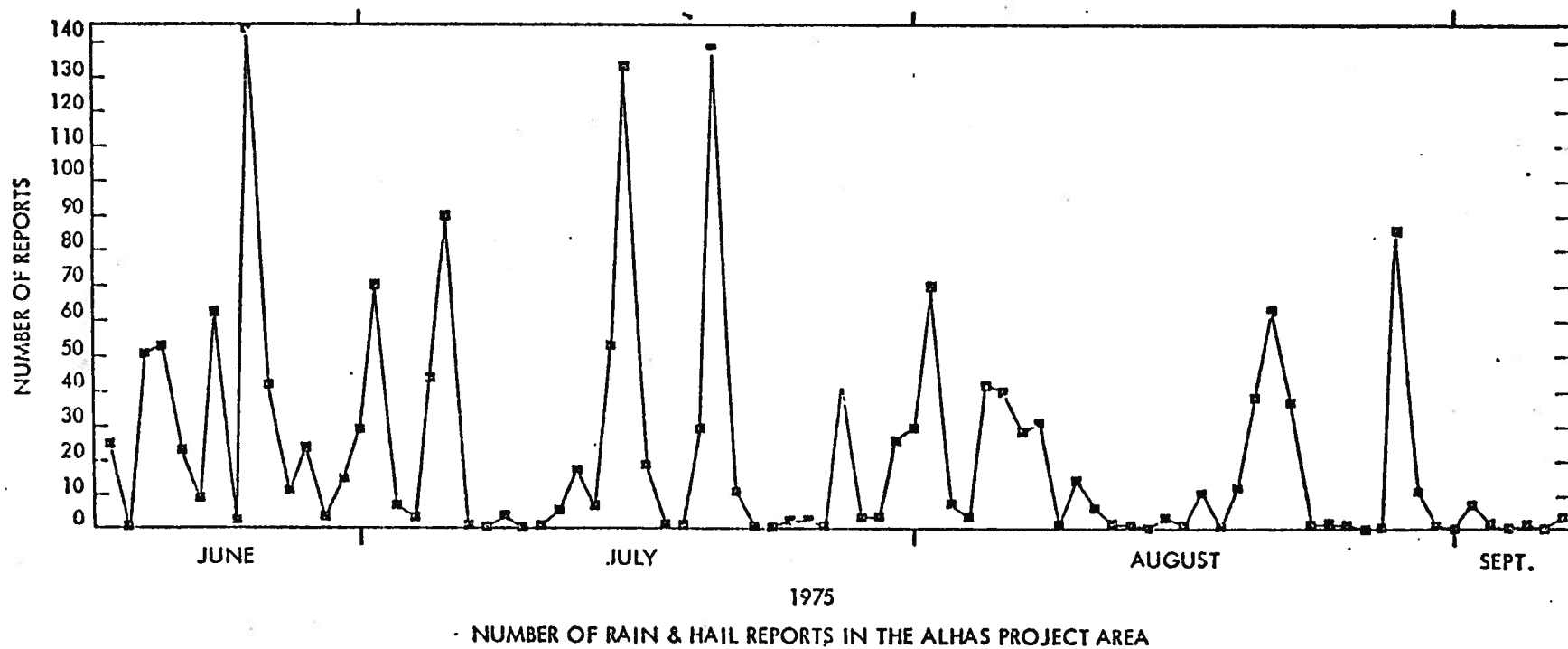
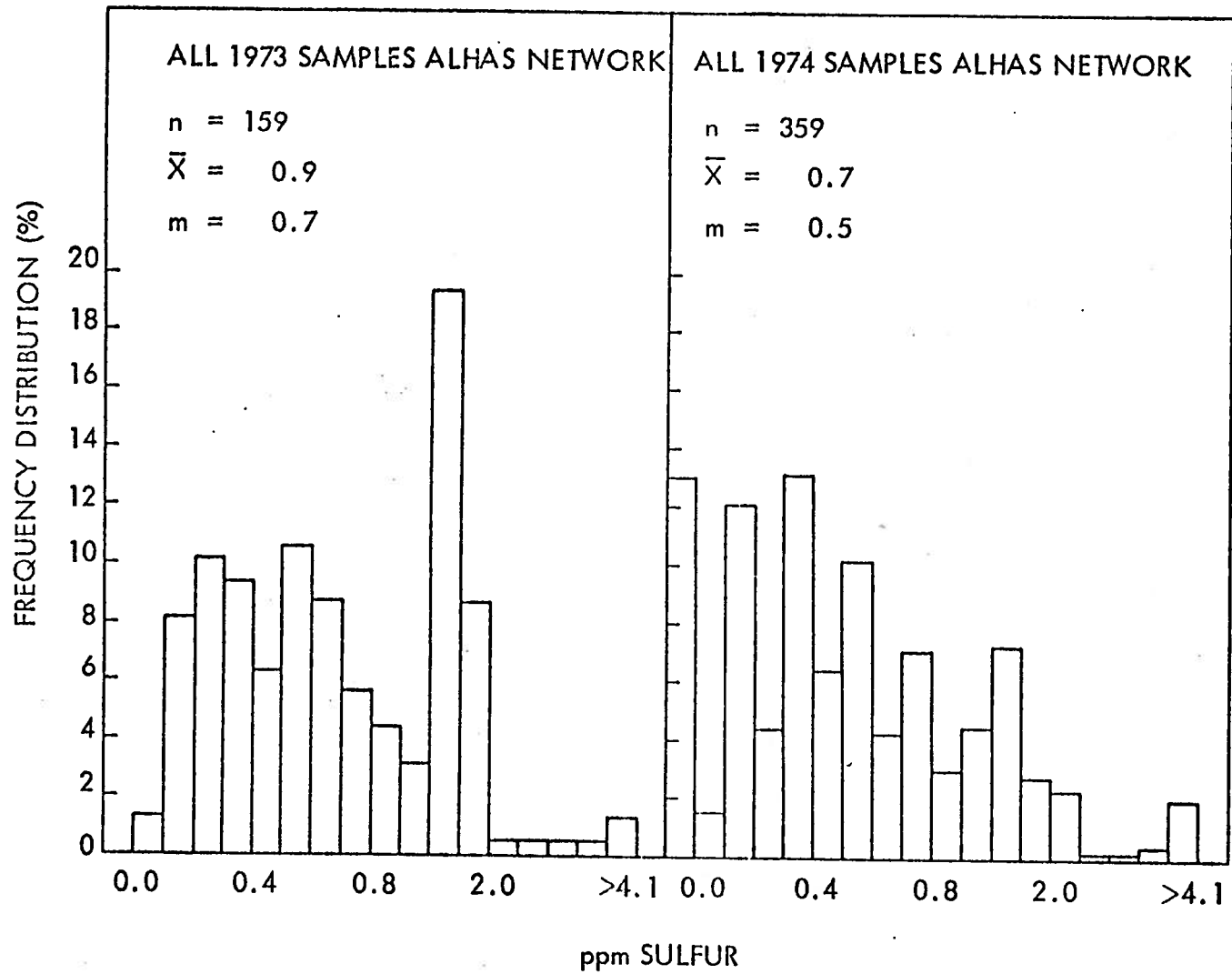


Figure 15: Frequency of rain and hail reports in the ALHAS project area, 1975



-Figure 16: Frequency distribution (%) of SO_4-S (ppm) in summer precipitation samples from ALHAS network, 1973 & 1974.

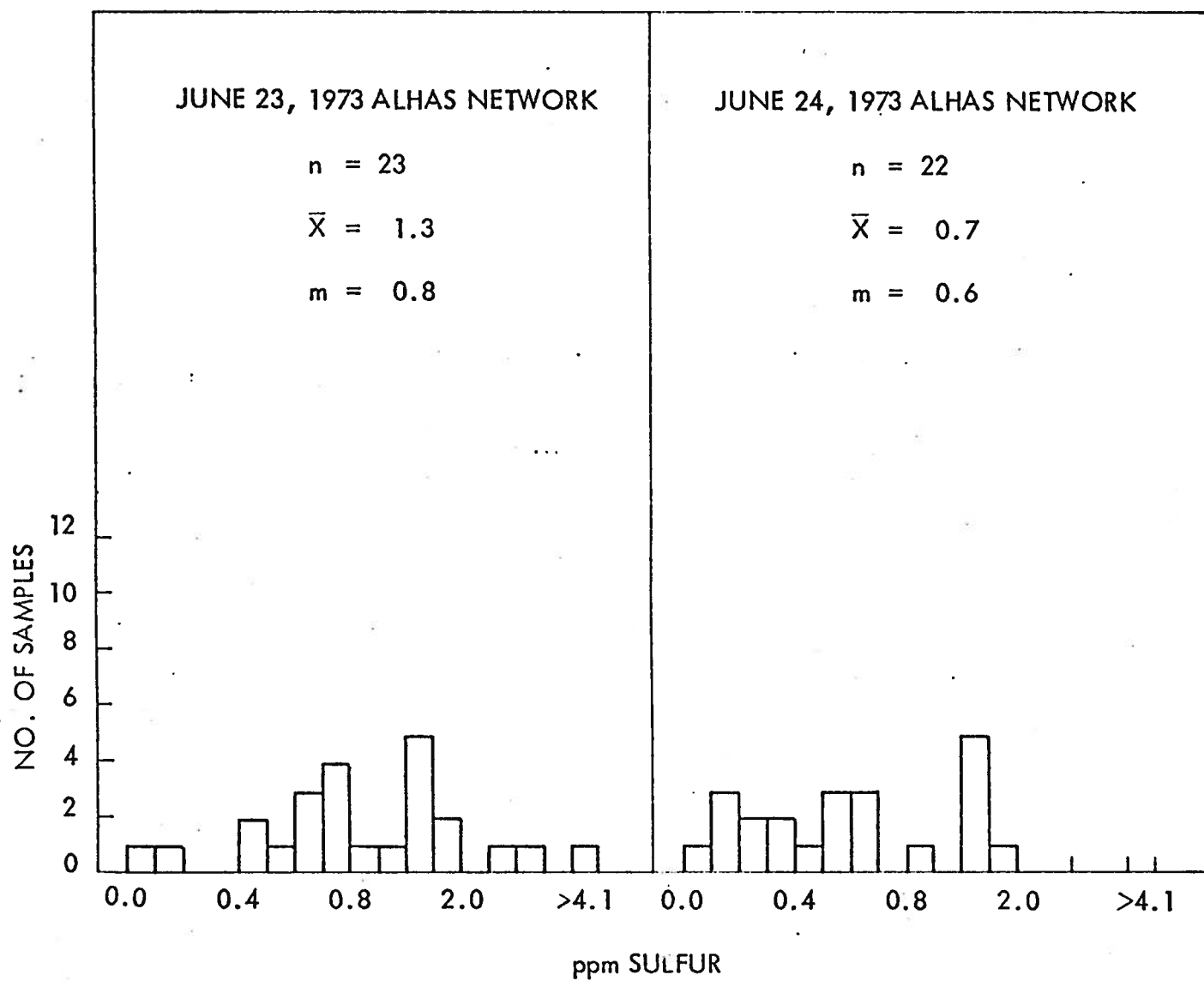


Figure 17: Distribution of SO_4-S values (ppm) for the indicated precipitation events.

n = no. of samples analysed
 \bar{X} = average value
 m = median value

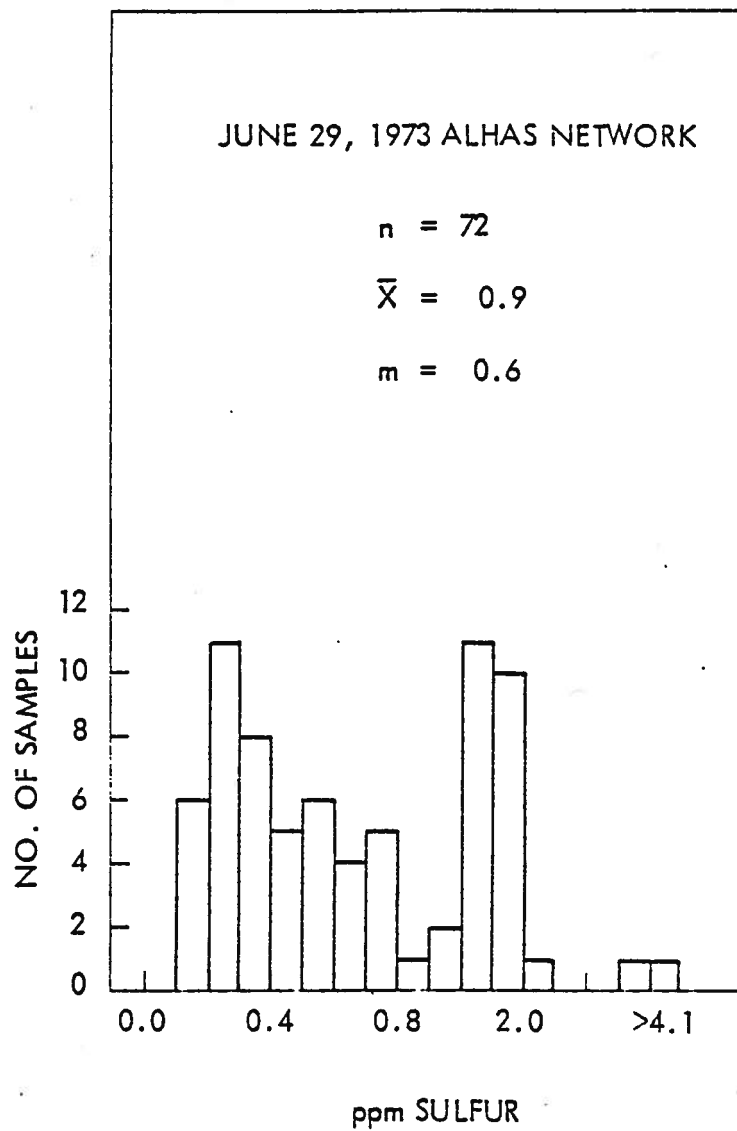


Figure 18: Distribution of $\text{SO}_4\text{-S}$ values (ppm) for the indicated precipitation events.

n = no. of samples analysed
 \bar{X} = average value
m = median value

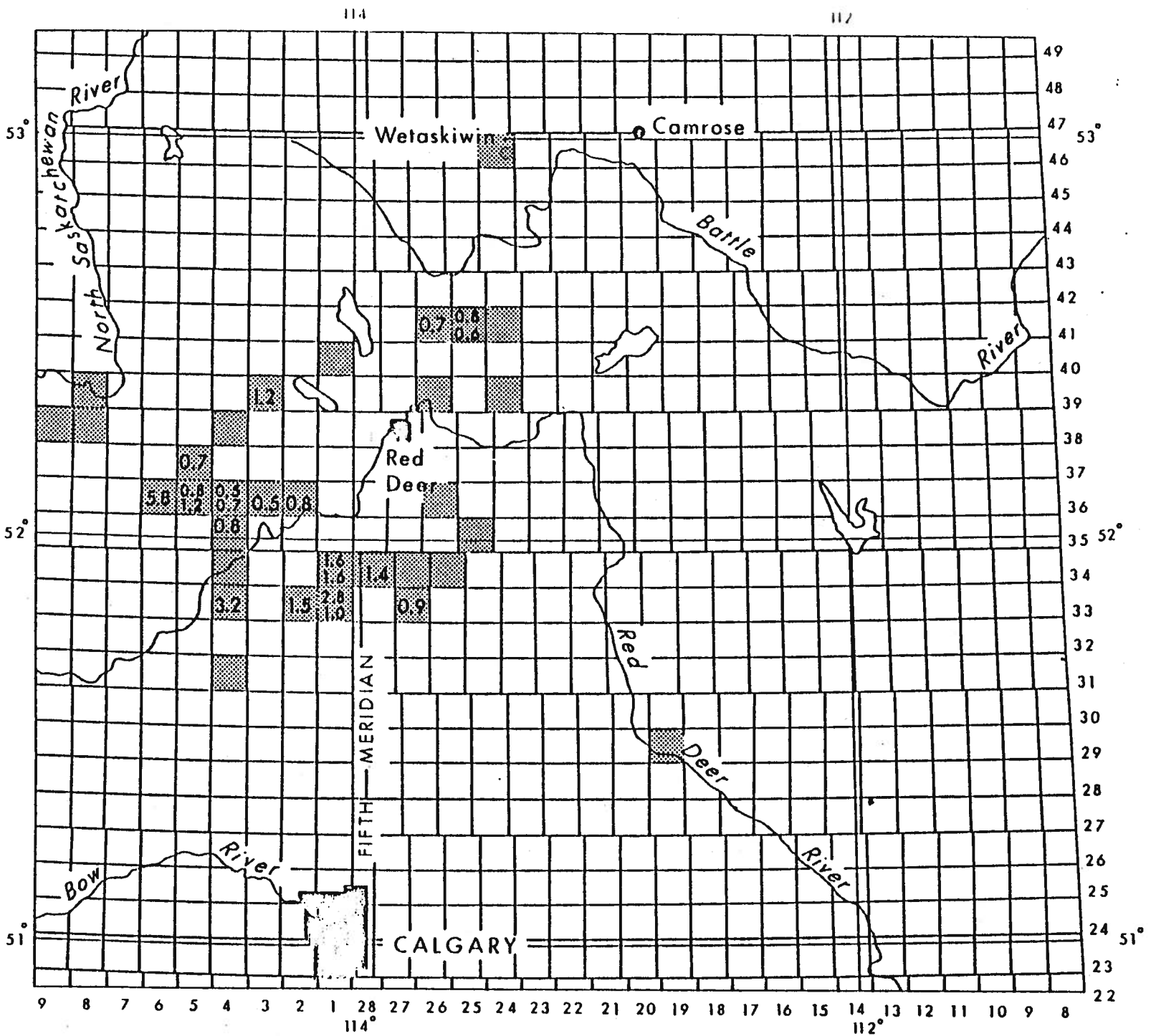


Figure 19: Geographical distribution of SO₄-S results for the precipitation event of June 23rd, 1973.

June 23, 1973

Although areas of similar onset time can be discerned for this event, it is impossible to pin point a 'storm front'. A tendency for an easterly flow of air on the east side of these onset areas can be identified. In addition air flow in a northerly direction is evident in the north eastern sector of the storm envelope. A very few reports of hail accompanied this storm. The area encompassed by this event contains only one sulfur plant of greater than 25 LTD and only one plant in the 5-24 LTD range. The high (3.2 and 2.8 ppm) $\text{SO}_4\text{-S}$ reports occurred at least 10 miles distant from these plants. Over 82% of the samples analysed were below 2 ppm $\text{SO}_4\text{-S}$. The construction of iso-lines of equal $\text{SO}_4\text{-S}$ value would be meaningless as onset of precipitation varied over 24 hours in the area under consideration.

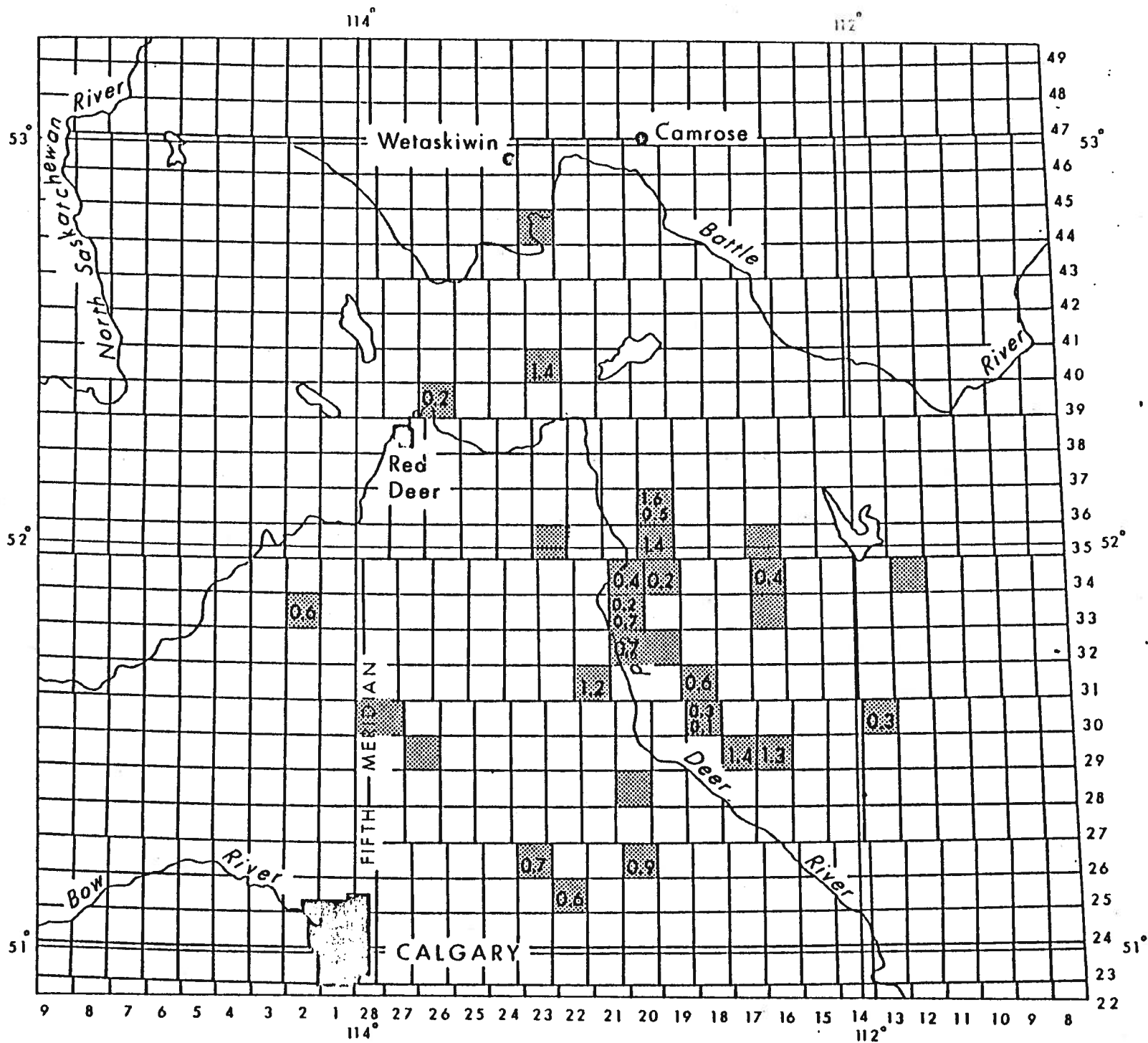


Figure 20: Geographical distribution of $\text{SO}_4\text{-S}$ results for the precipitation event of June 24th, 1973.

June 24, 1973

This was a gentle, long rain 25 miles distant from the nearest sulfur emitter and moving in a north-south direction. One phase of this event began early in the morning, with a second rain beginning after 1 p.m. $\text{SO}_4\text{-S}$ values are, on the whole, lower than those of the previous day. Under the circumstances it has been judged that no sulfur plants contributed emissions to this event.

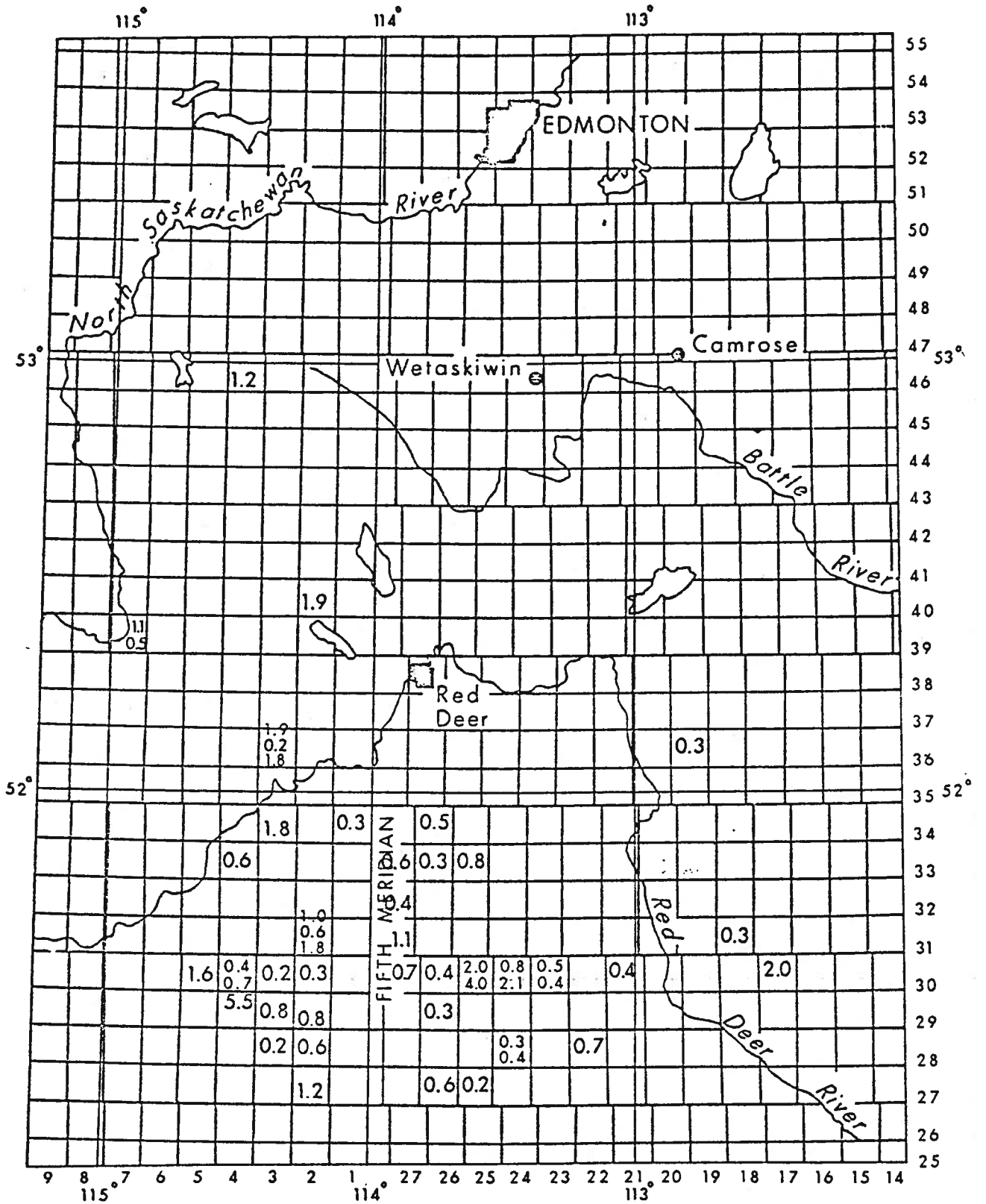


Figure 21: Geographical distribution of SO₄-S results (ppm) for the precipitation event of June 29th, 1973.

June 29, 1973

A storm began south west of Didsbury. Another storm cell appears to have begun about 35 miles due north. These cells then combined to move south-east on a 60 mile front at a rate of about 12 mph. There is an indication that high sulfur iso-lines correlate with the appearance of the storm front, i.e. early phases of the storm associated with high $\text{SO}_4\text{-S}$ in precipitation. This was particularly evident at the origins of the storm. The pattern of $\text{SO}_4\text{-S}$ values obtained was not well related to the location or size of the various sulfur emitters. Generally the rain at a given location within the path of the storm was of less than 30 minutes duration even though the storm began at 6 p.m. and lasted until midnight. Once again 92% of the samples analyzed below 2 ppm $\text{SO}_4\text{-S}$, making depiction of $\text{SO}_4\text{-S}$ isopleths a tenuous proposition.

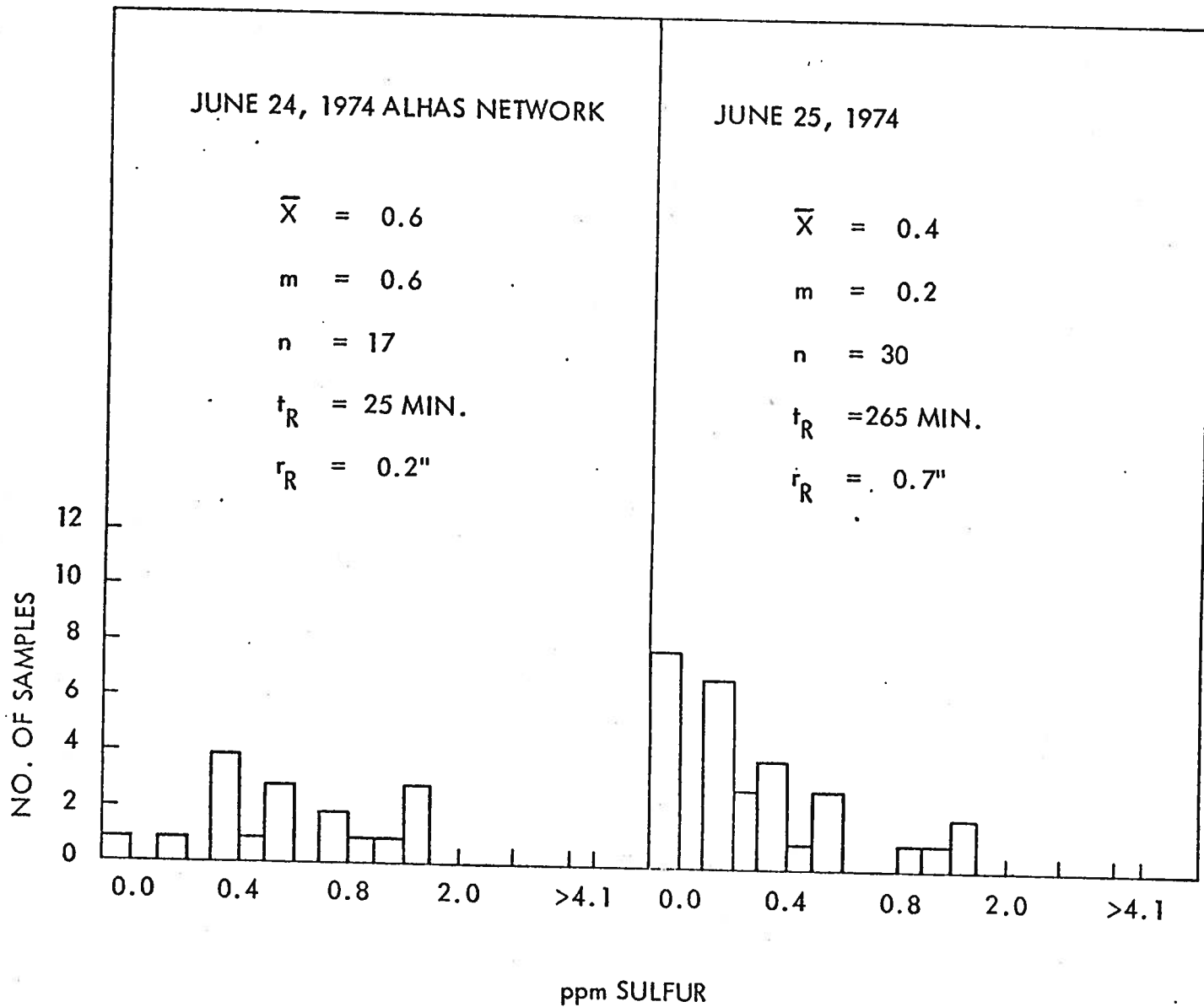


Figure 22: Distribution of $\text{SO}_4\text{-S}$ values (ppm) for the indicated precipitation events.

\bar{X} = average value

m = median value

n = no. of samples analysed

t_R = average duration of rainfall

r_R = average total rainfall, in inches

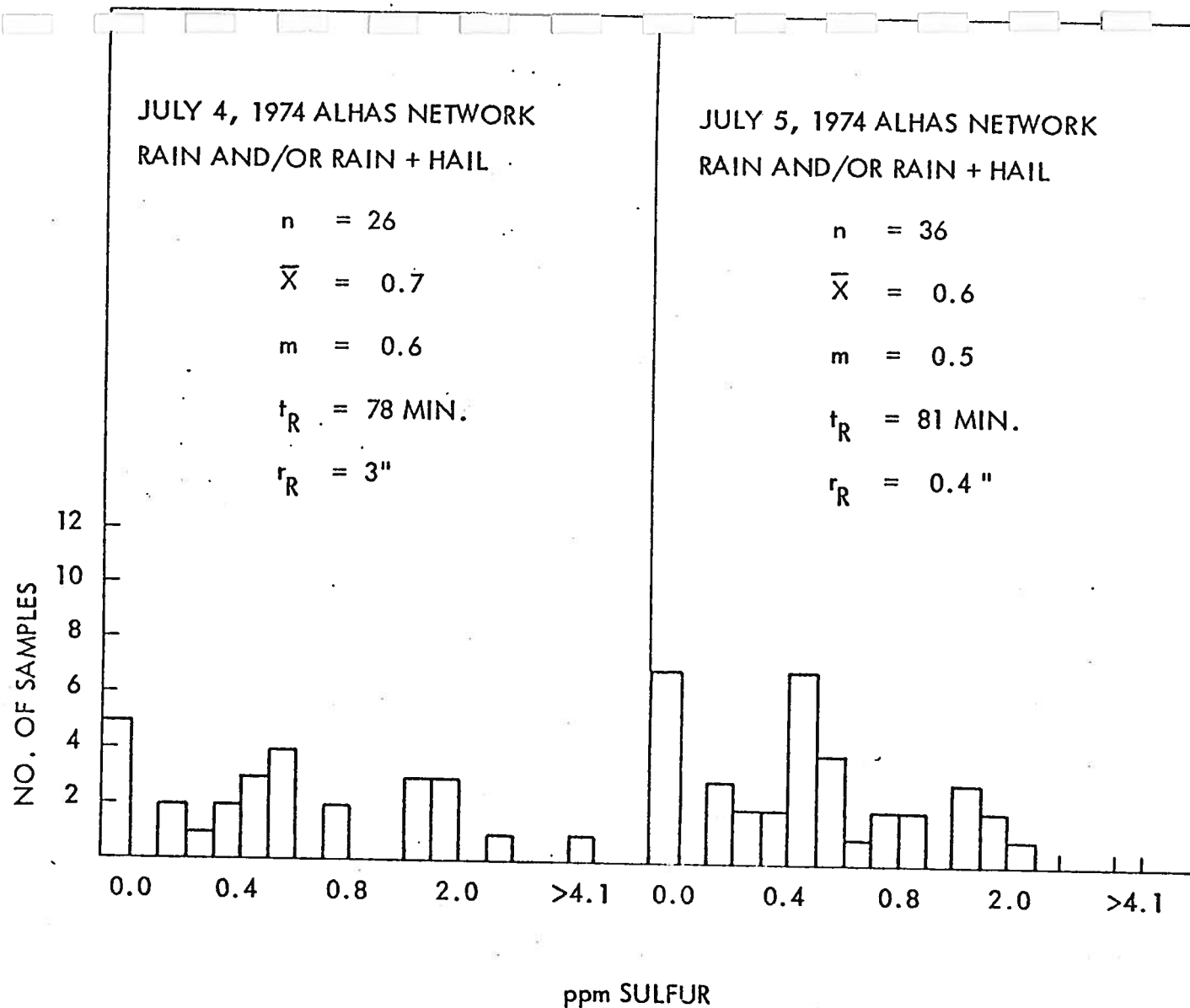


Figure 23: Distribution of SO_4-S values (ppm) for the indicated precipitation events.

n = no. of samples analysed

\bar{X} = average value

m = median

t_R = average duration of rainfall

r_R = average total rainfall, in inches

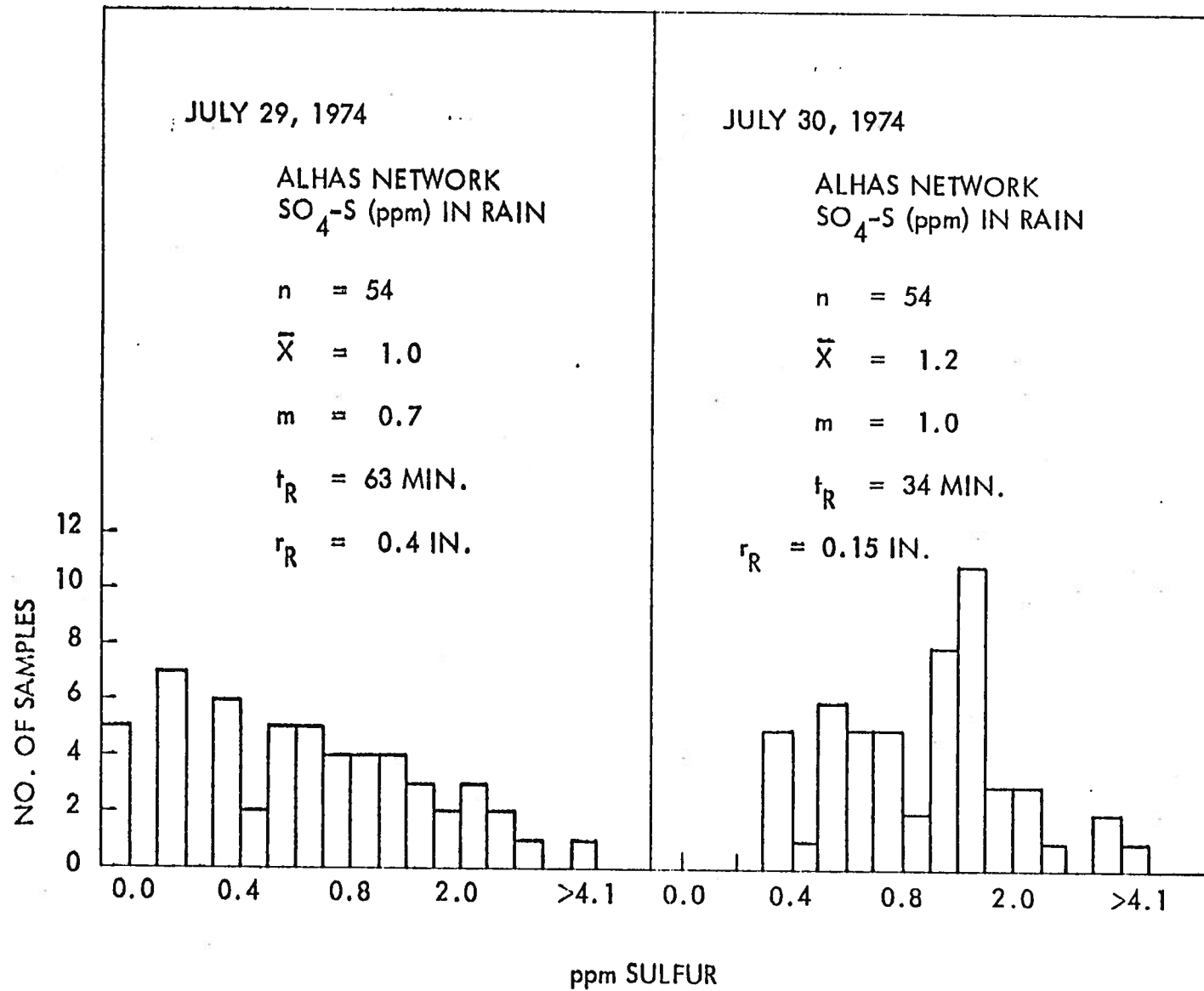


Figure 24: Distribution of SO₄-S values (ppm) for the indicated precipitation events.

n = no. of samples analysed
 \bar{X} = average value
 m = median

t_R = average duration of
rainfall
 r_R = average total rainfall,
in inches

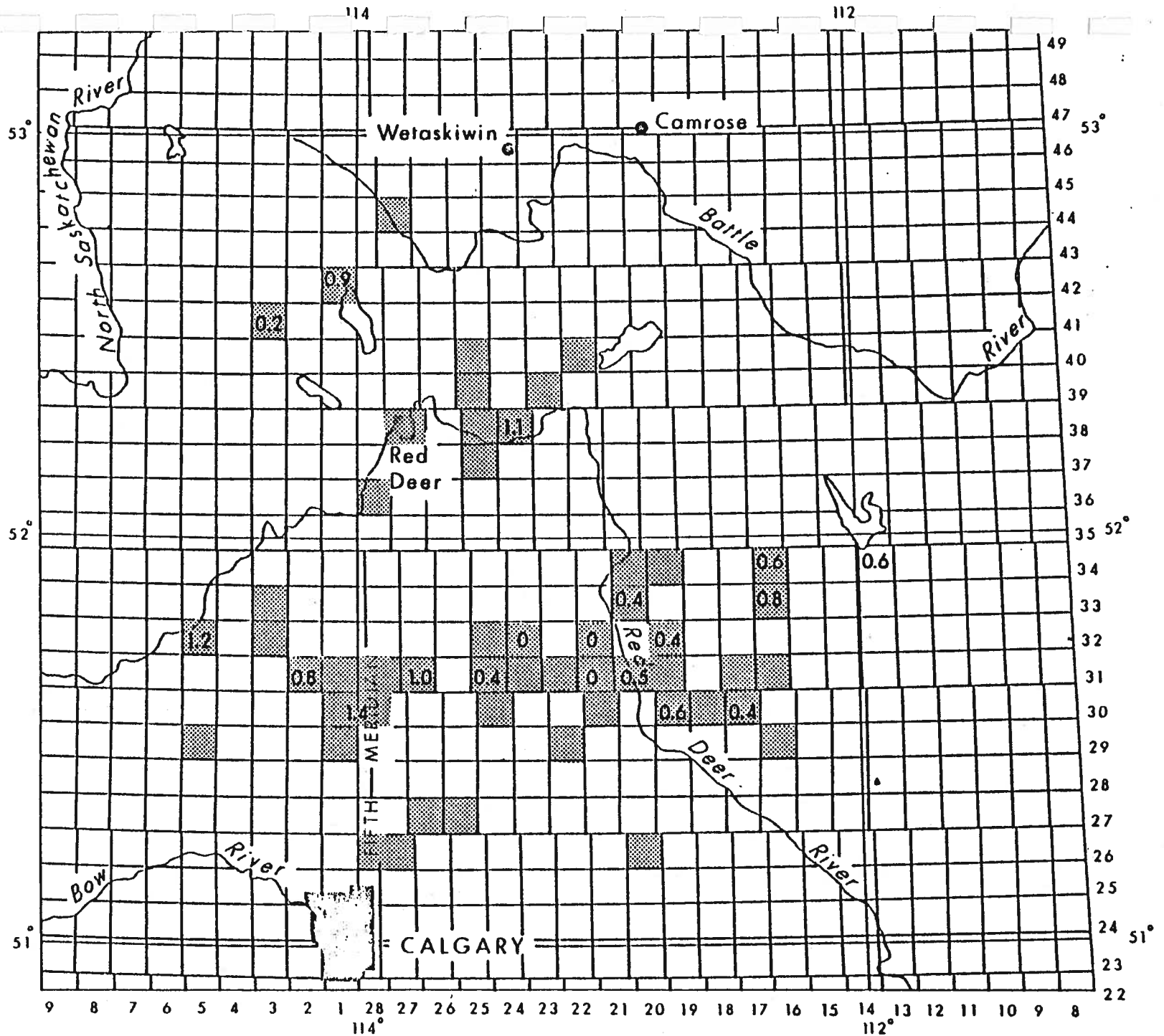


Figure 25: Geographical distribution of $\text{SO}_4\text{-S}$ results (ppm) for the precipitation event of June 27/28, 1976.

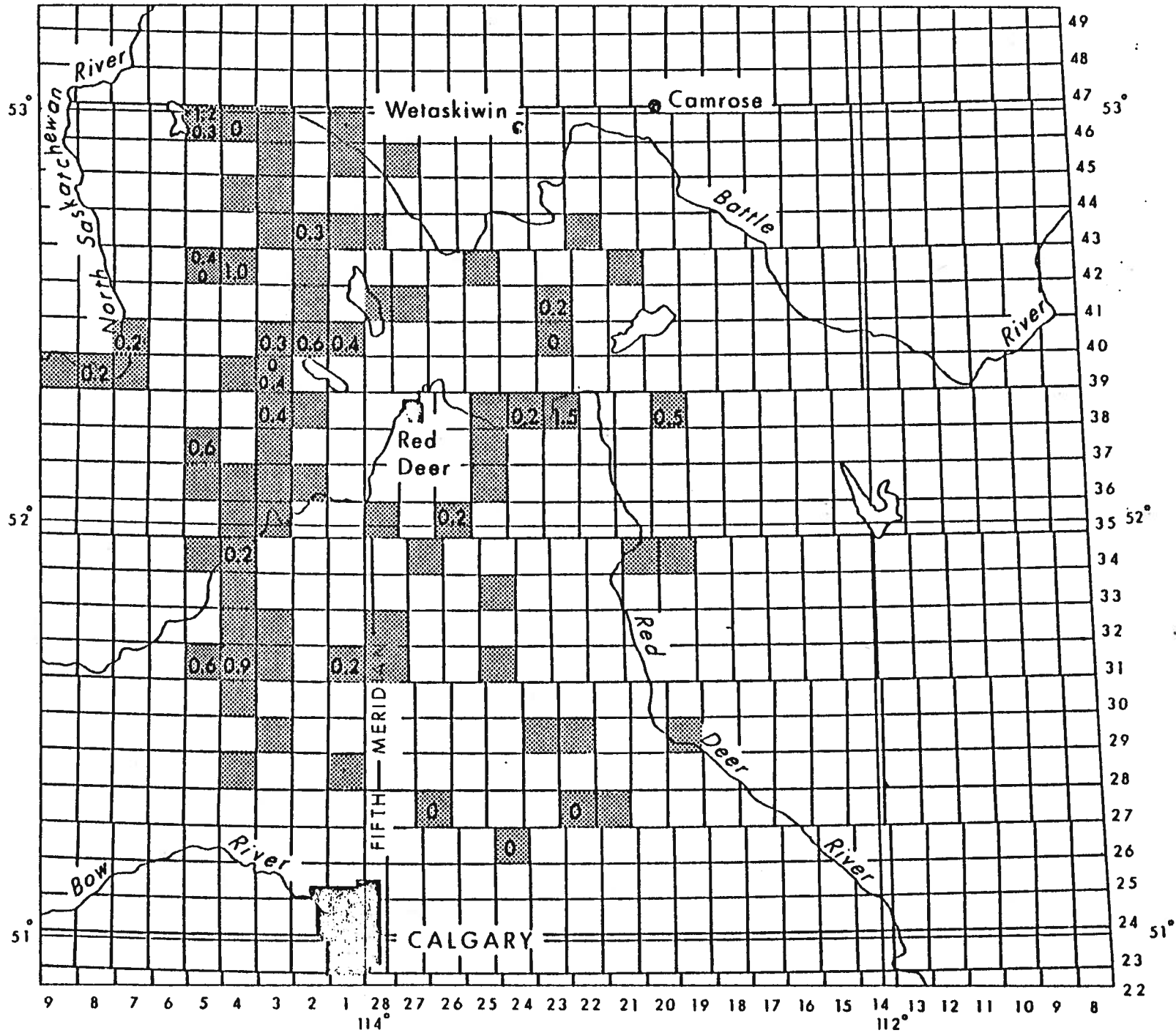


Figure 26: Geographical distribution of SO₄-S results (ppm) for the precipitation event of June 25, 1974.

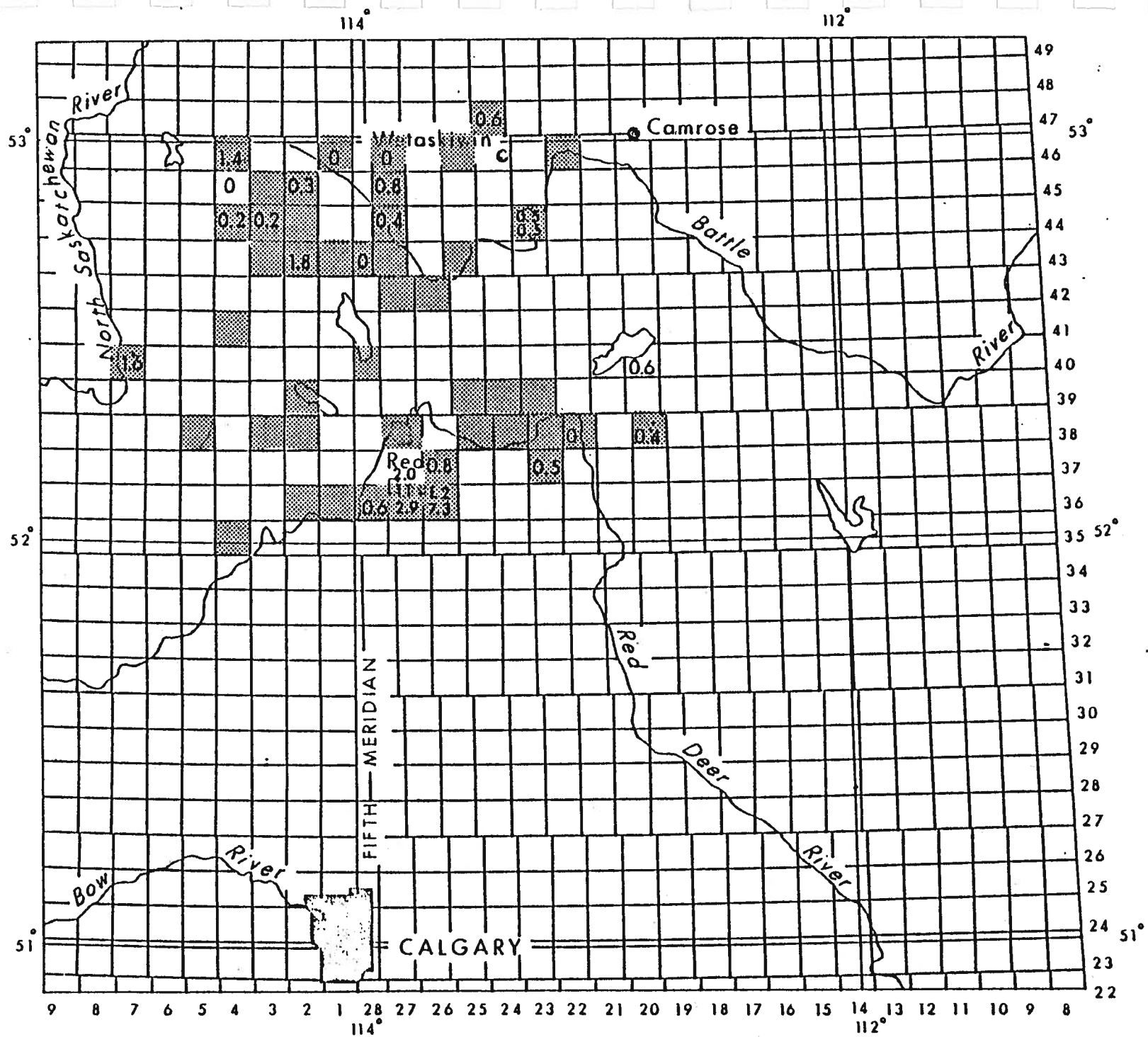


Figure 27: Geographical distribution of $\text{SO}_4\text{-S}$ results (ppm) for the precipitation event of July 4th, 1974.

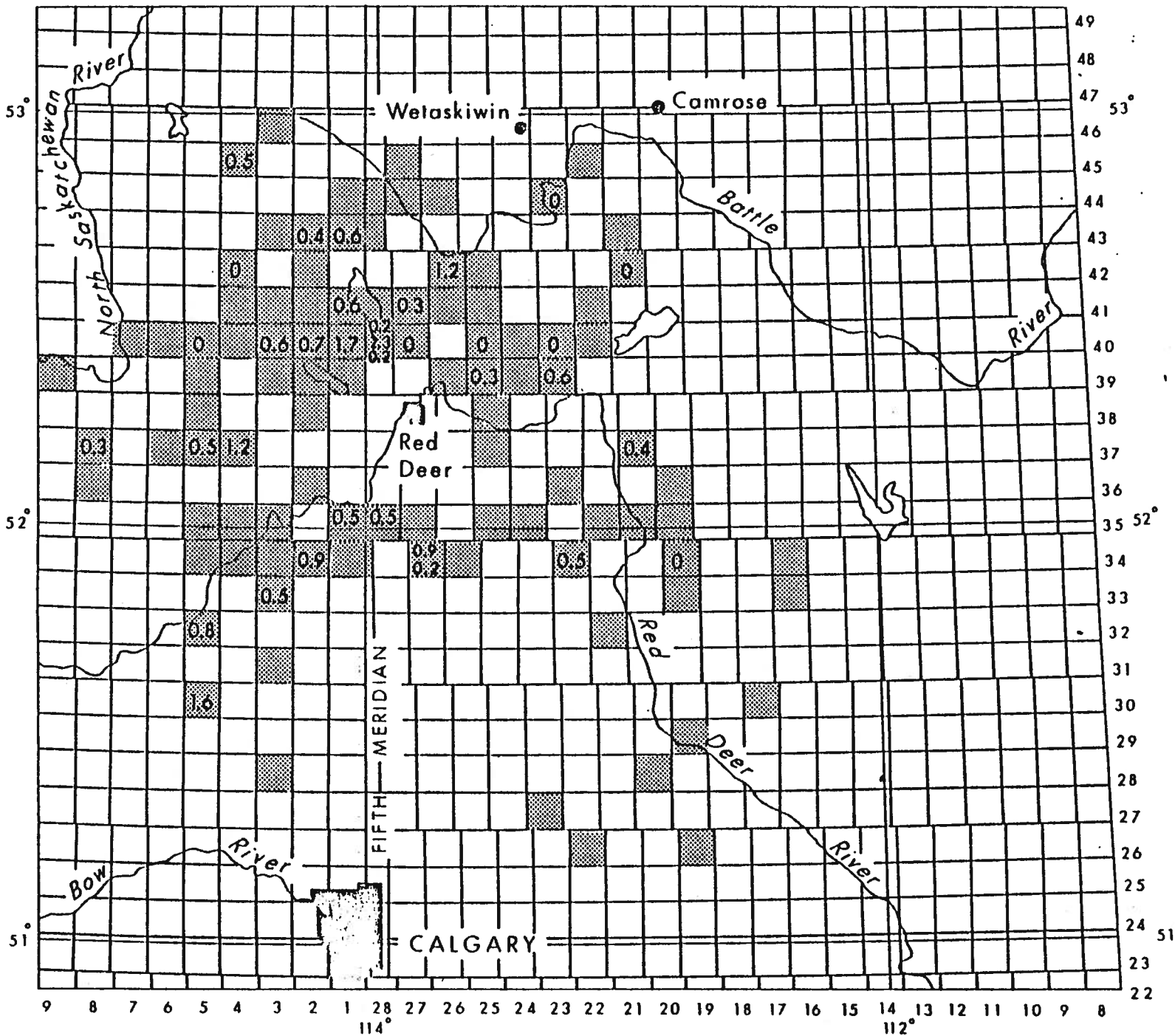


Figure 28: Geographical distribution of $\text{SO}_4\text{-S}$ results (ppm) for the precipitation event of July 5th, 1974.

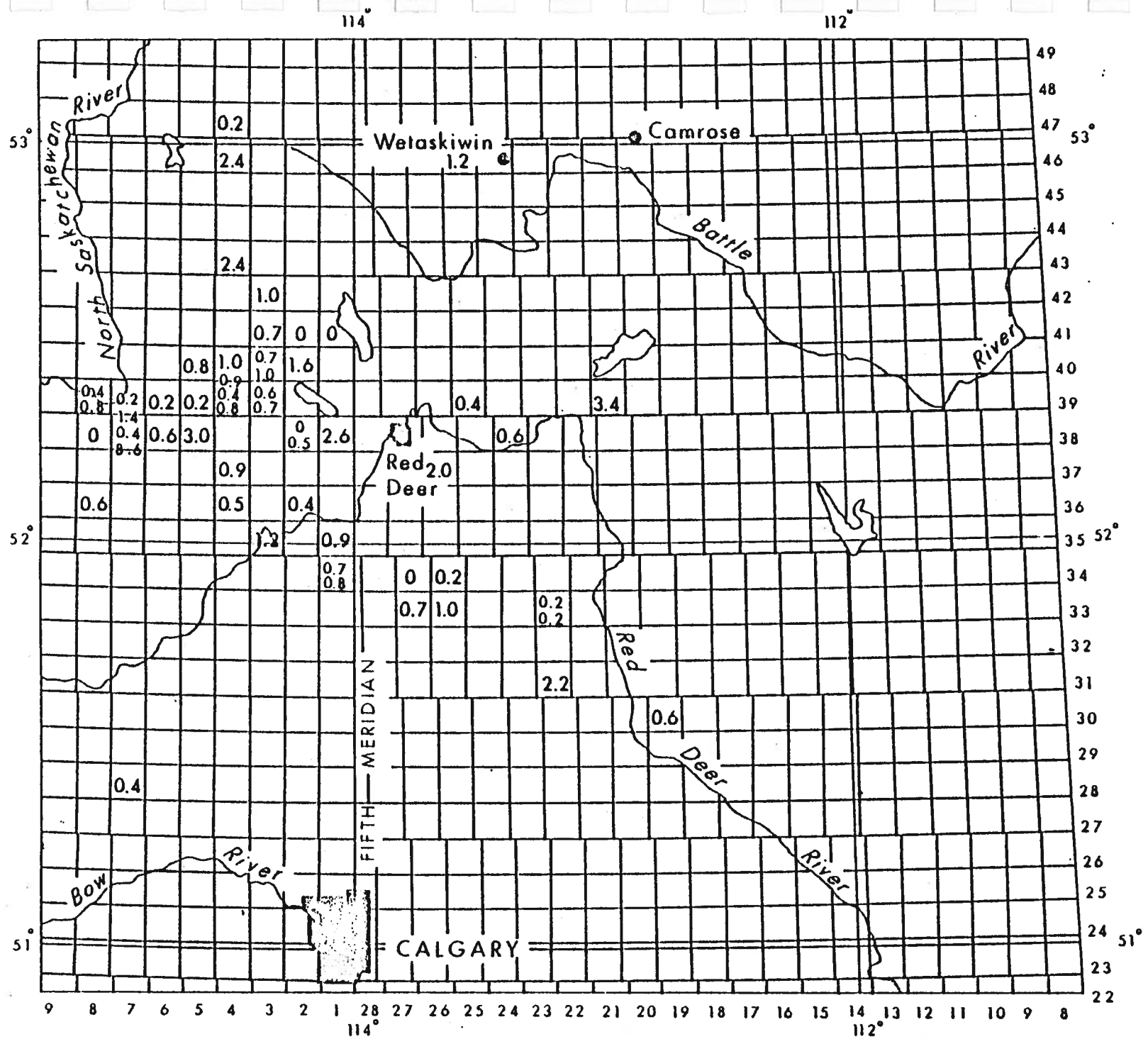


Figure 29: Geographical distribution of $\text{SO}_4\text{-S}$ results (ppm) for the precipitation event

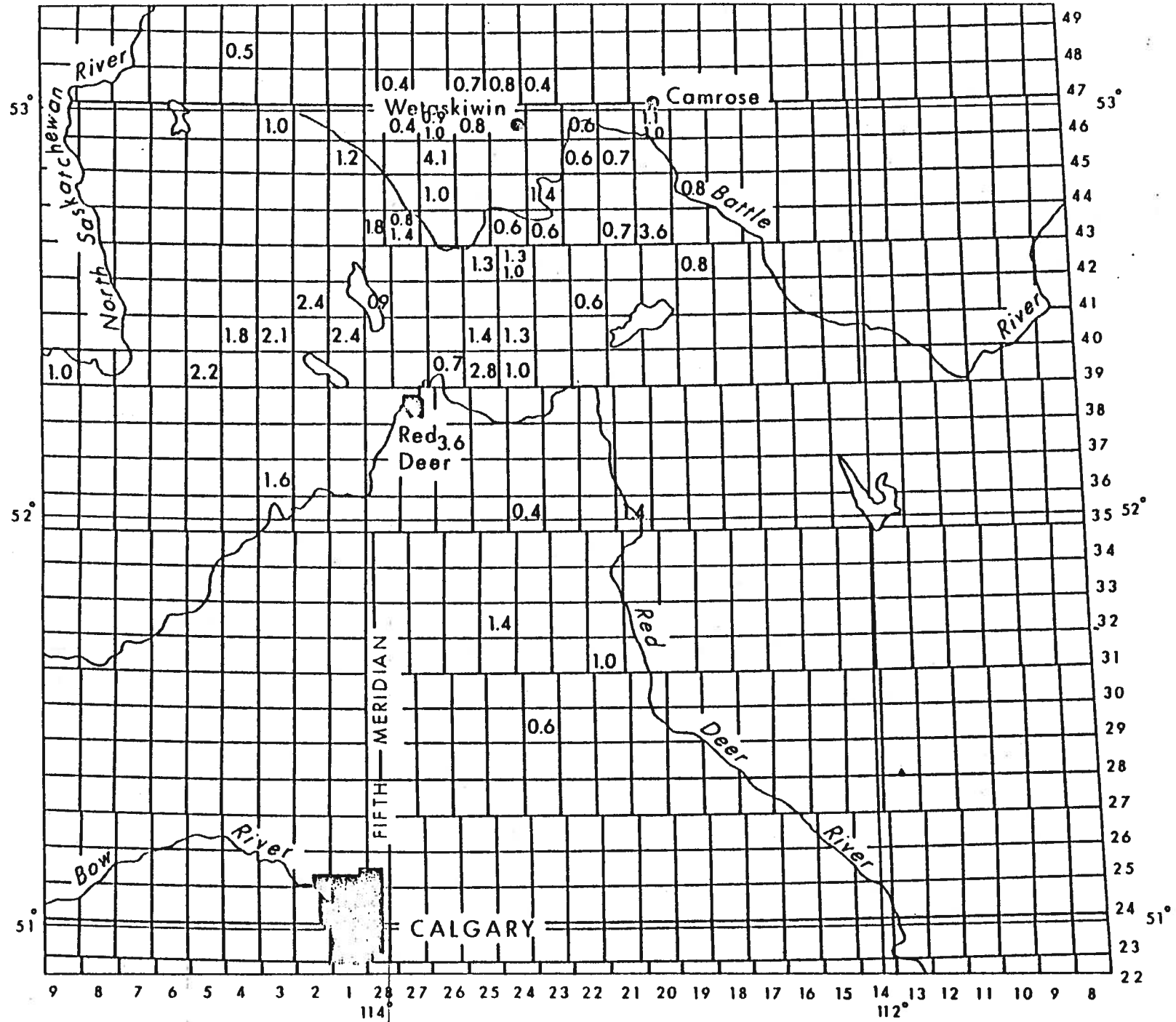


Figure 30: Geographical distribution of $\text{SO}_4\text{-S}$ results (ppm) for the precipitation event of July 30th, 1974.

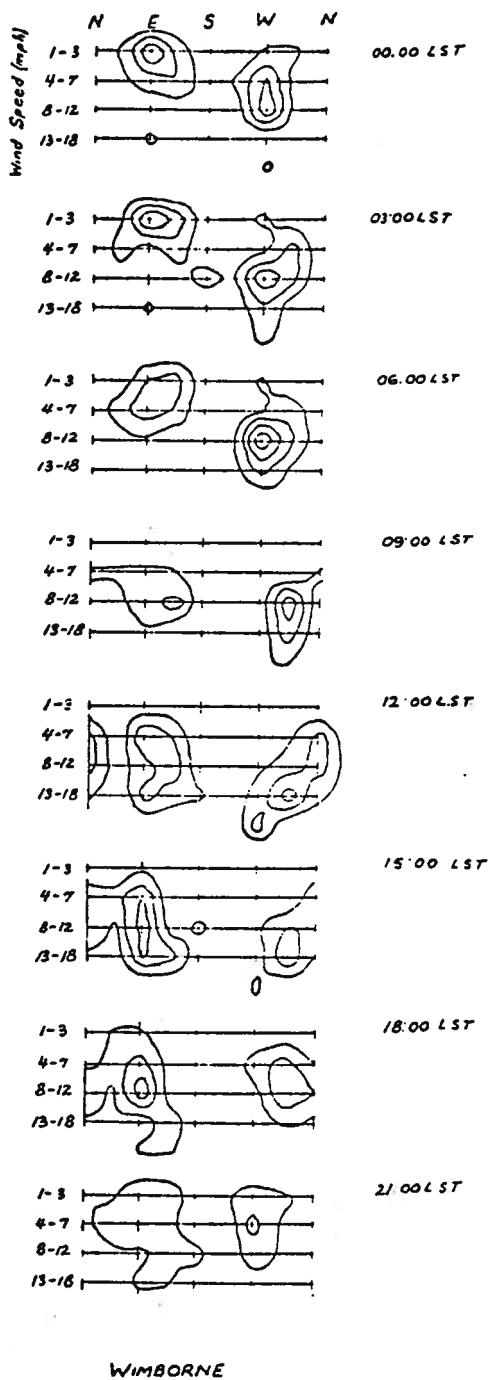


Figure 31: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. May, 1975.

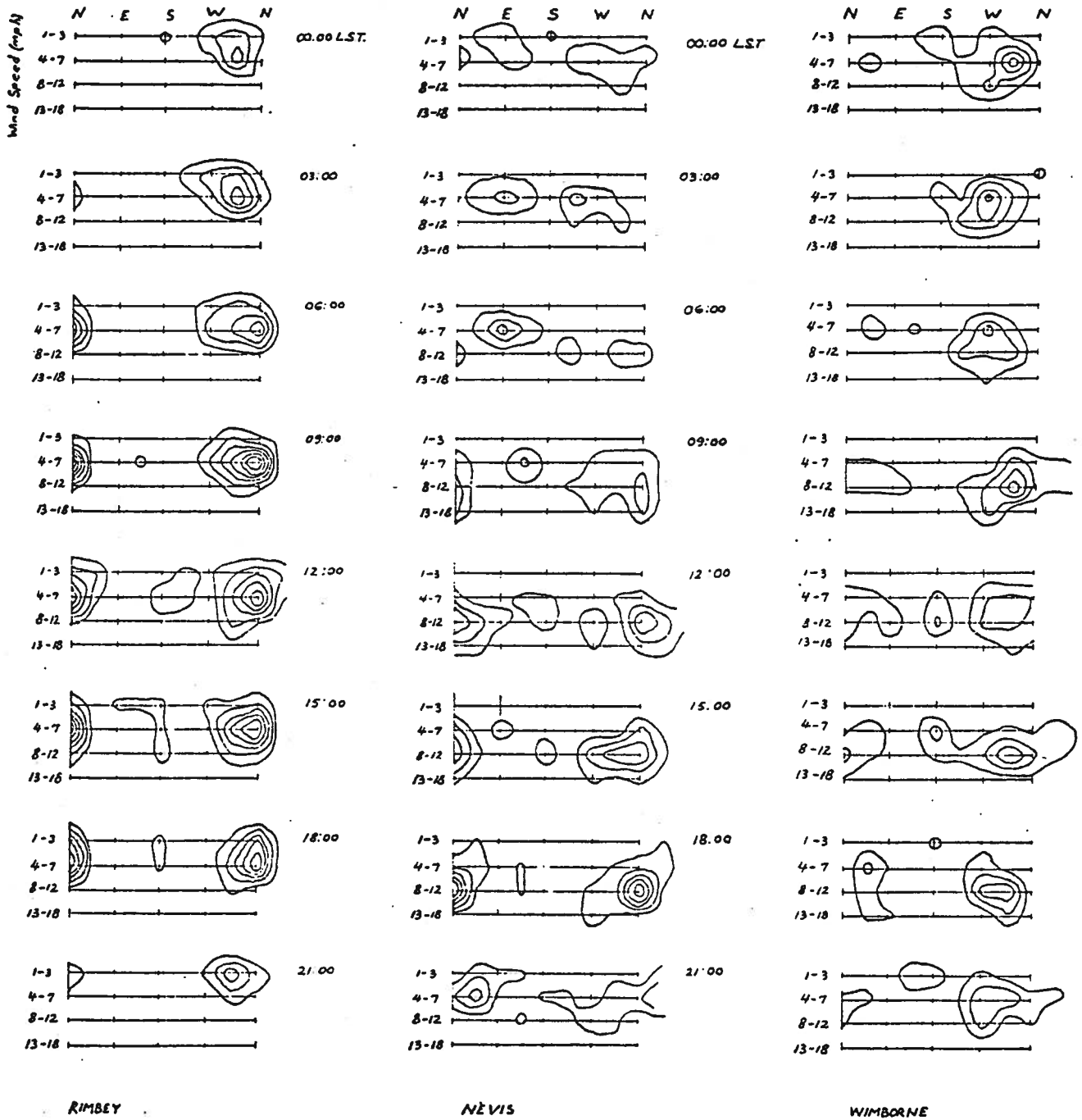


Figure 32: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. June, 1975.

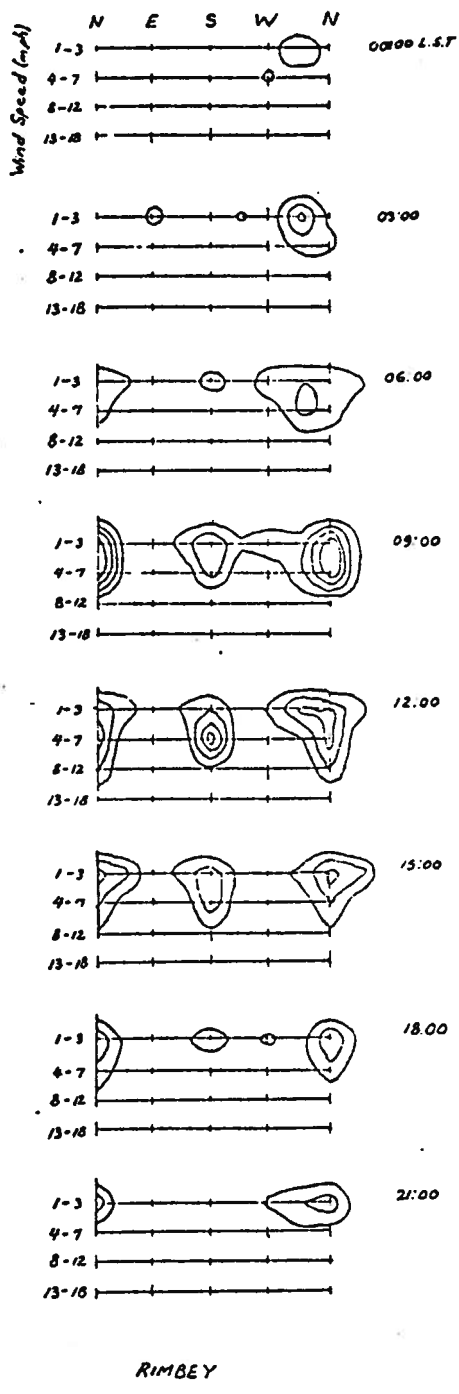


Figure 33: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. RimbeY, July, 1975.

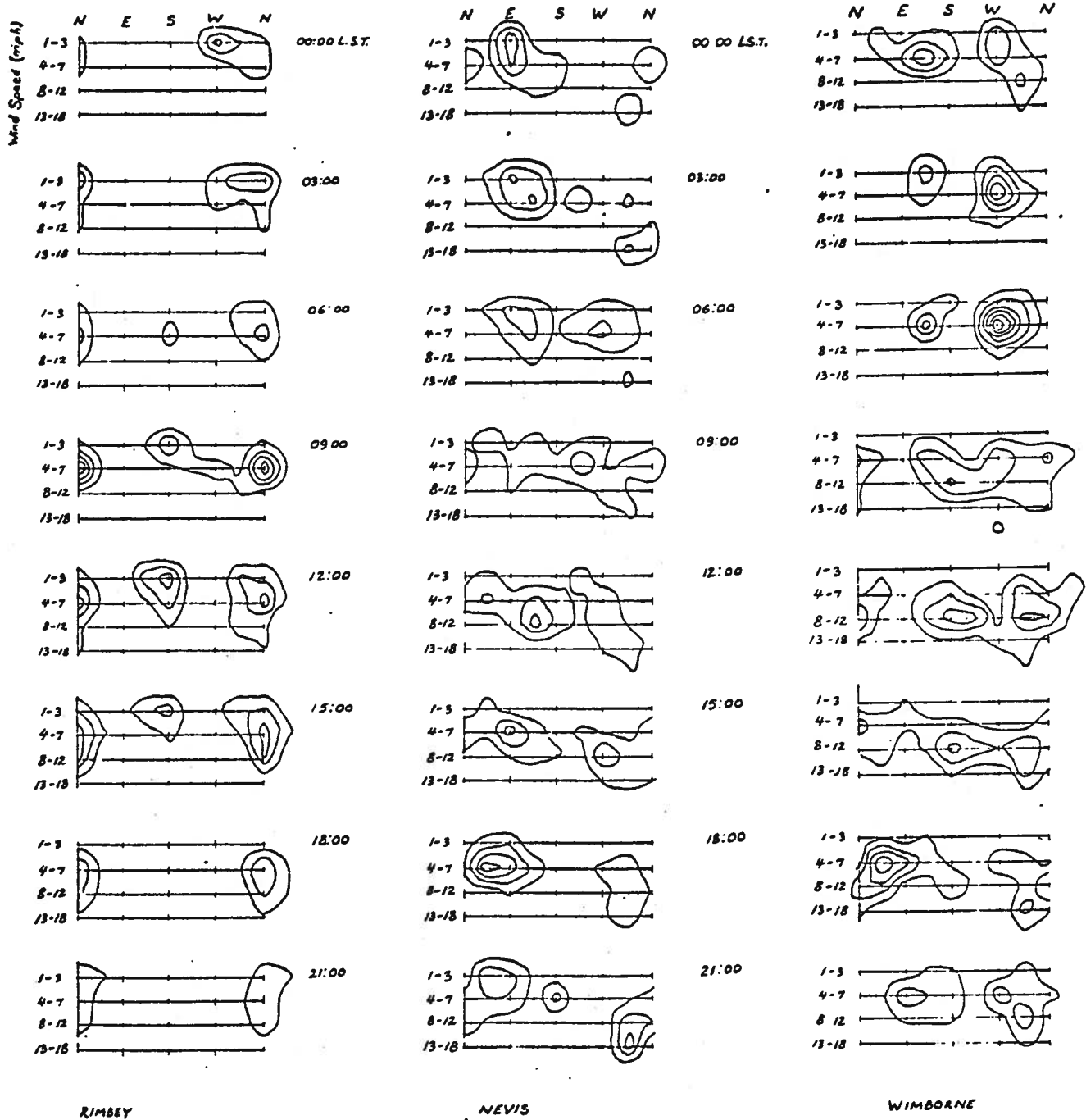


Figure 34: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. August, 1975.

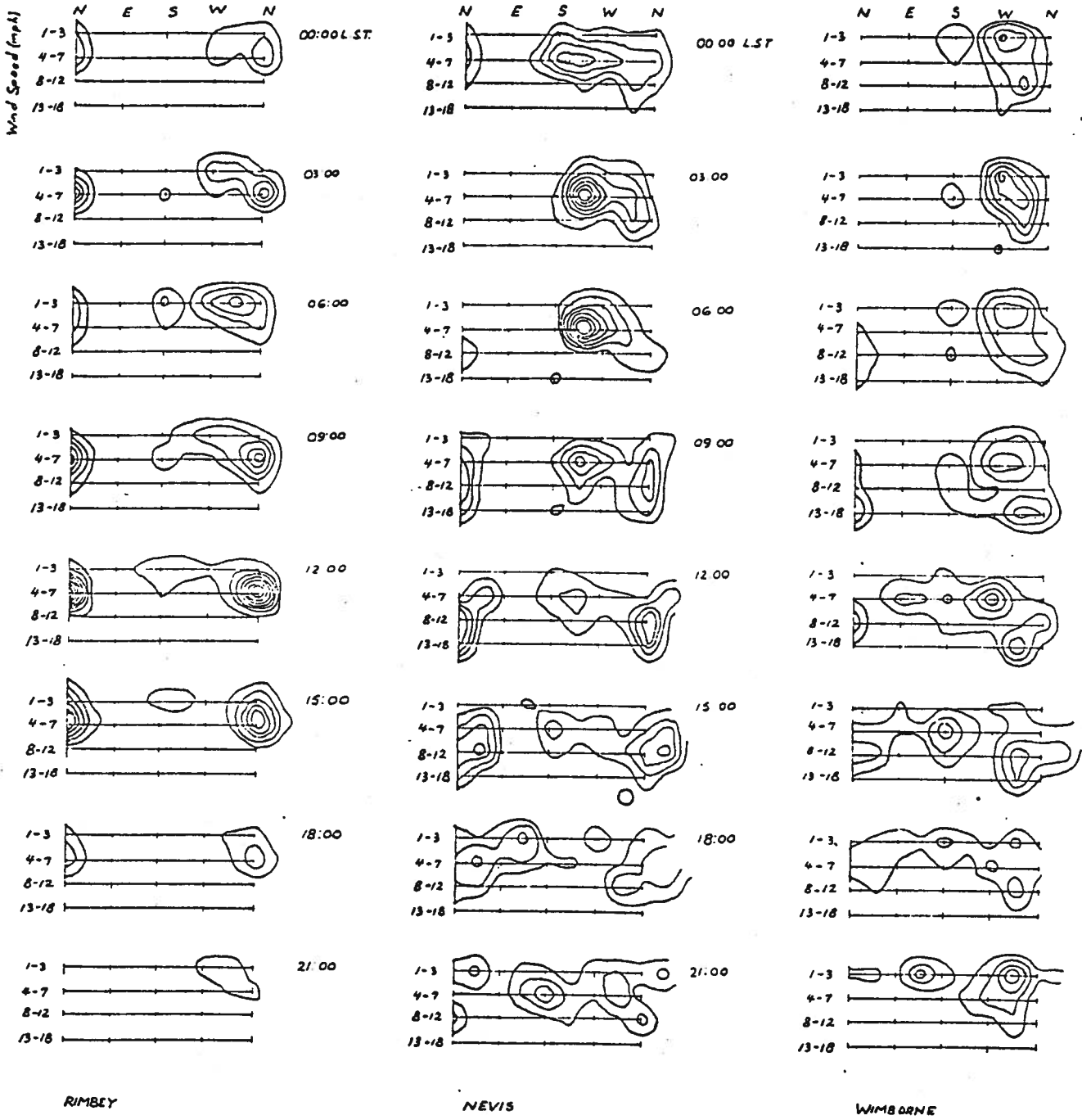


Figure 35: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. September, 1975.

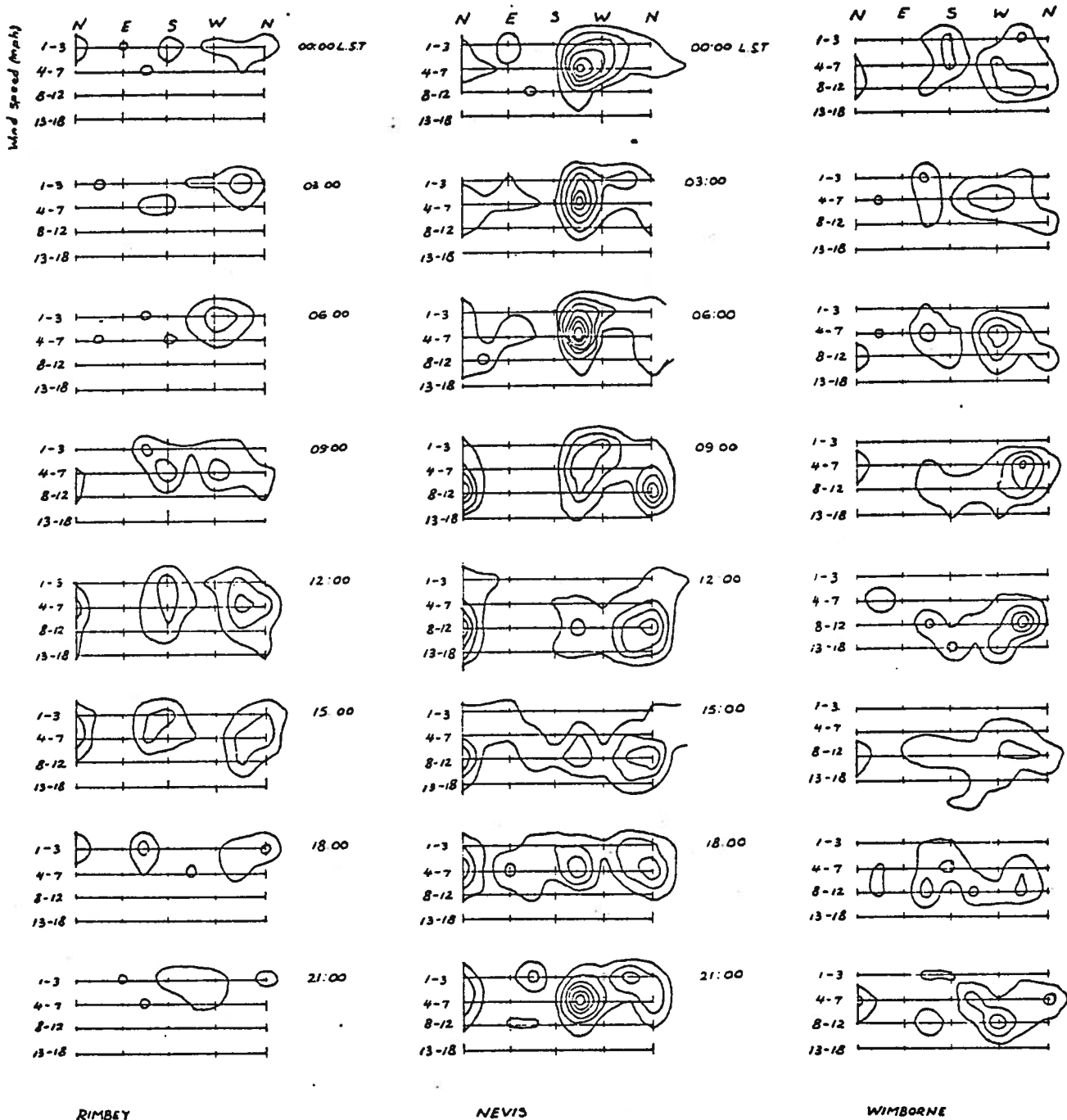


Figure 36: Iso-lines of the number of occasions that surface winds blew from each of the 16 compass points and within each of the speed ranges noted. October, 1975

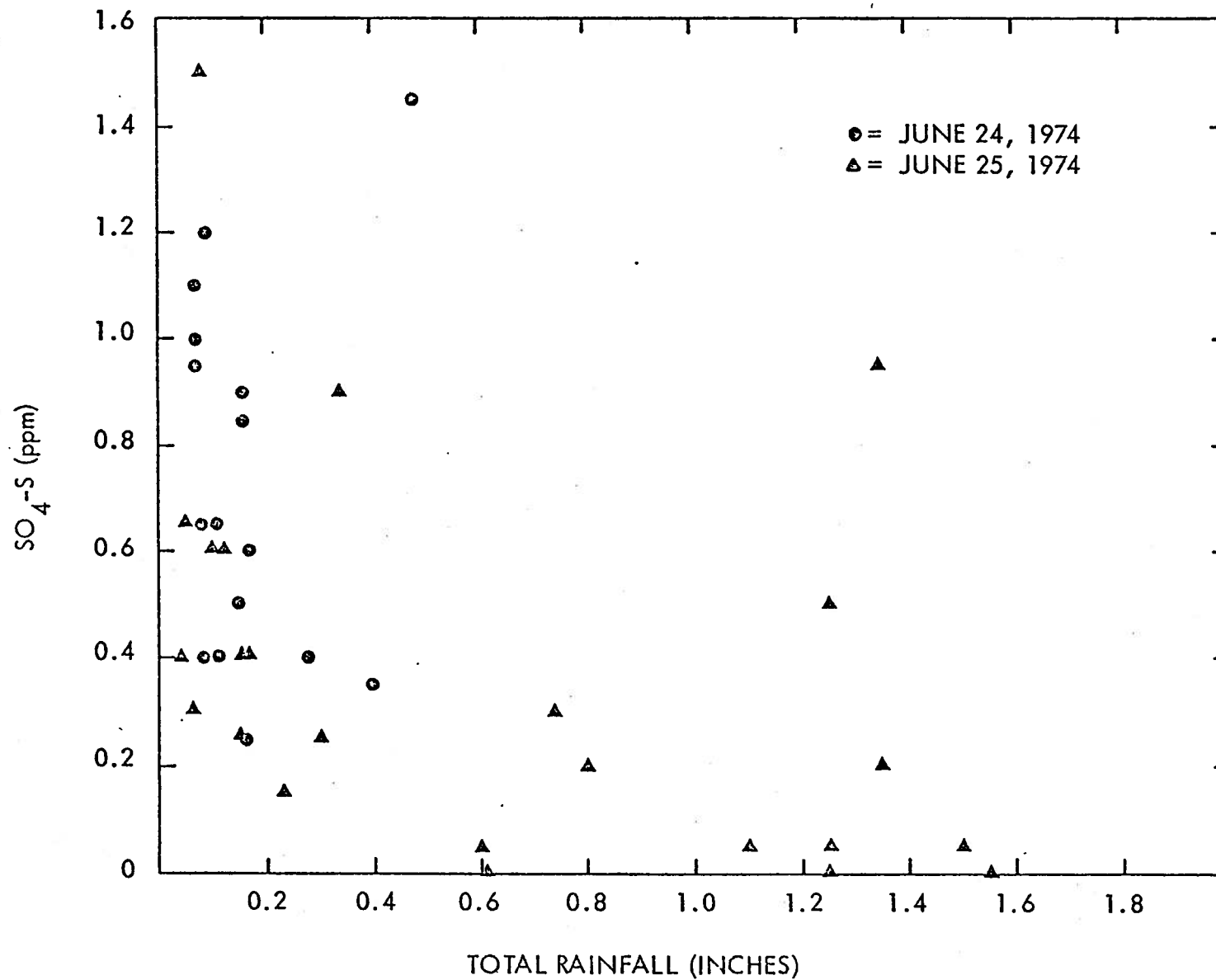


Figure 37: Concentration of SO₄-S (ppm) in precipitation as a function of the amount of rainfall.

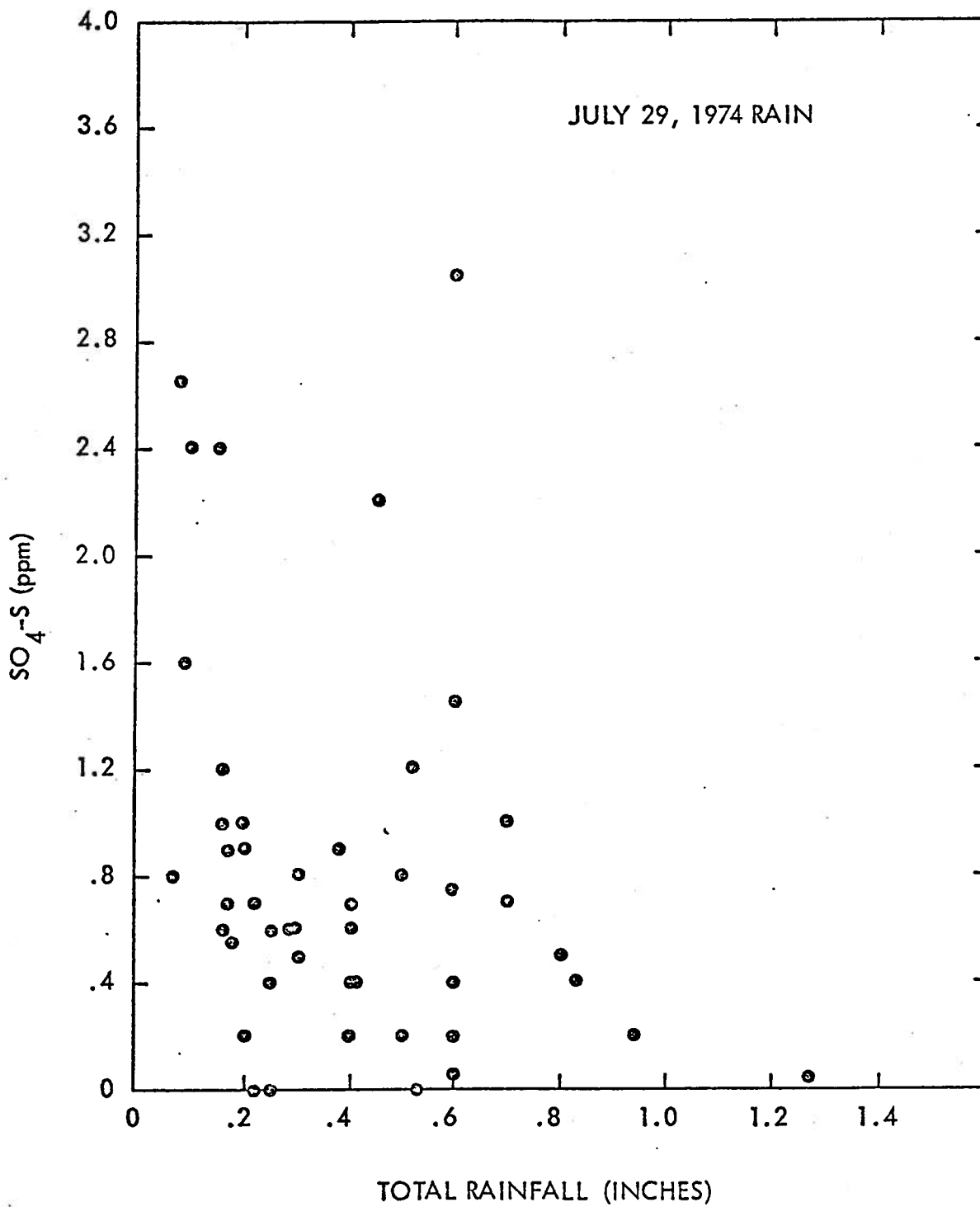


Figure 38: Concentration of SO₄-S (ppm) in precipitation as a function of the amount of rainfall.

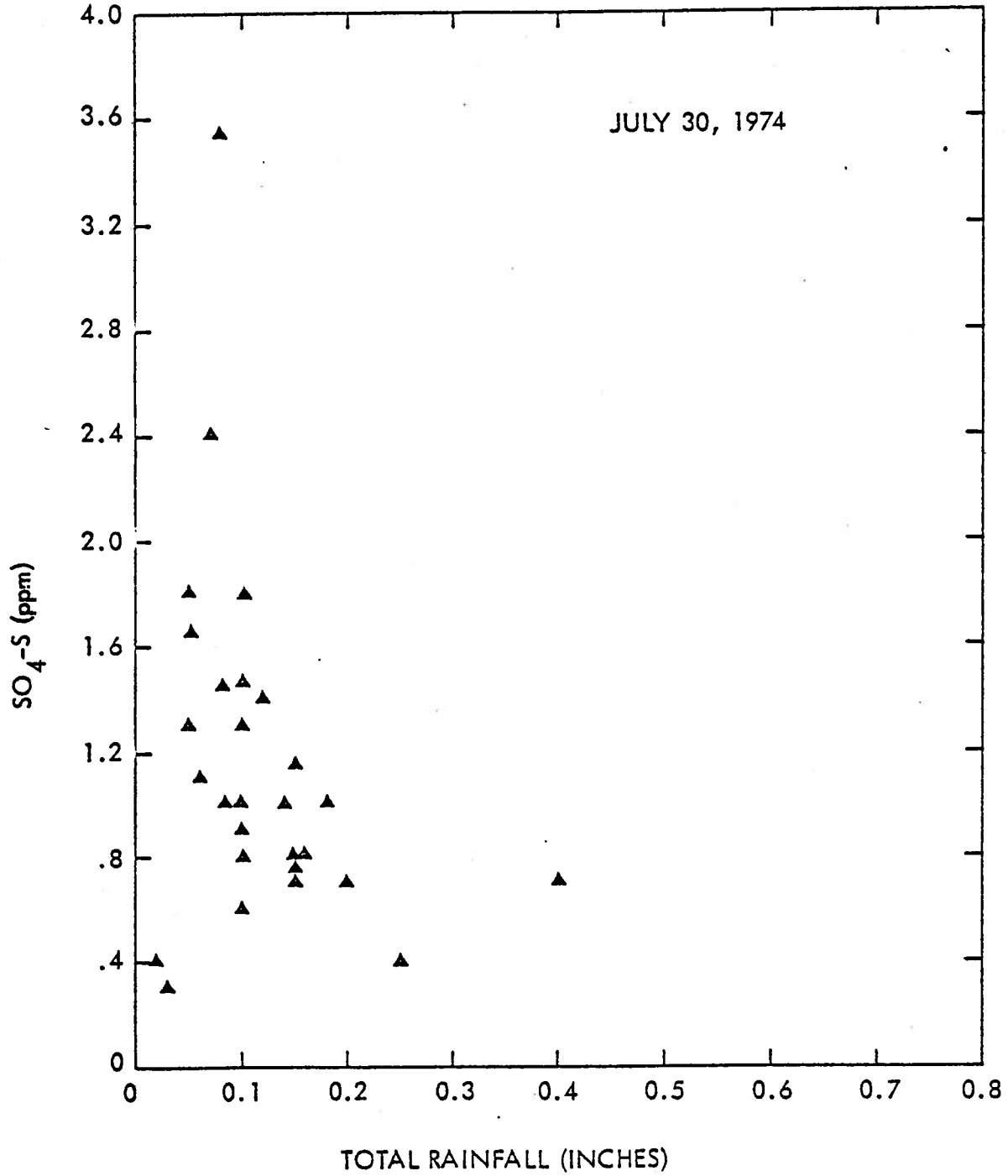


Figure 39: Concentration of $\text{SO}_4\text{-S}$ (ppm) in precipitation as a function of the amount of rainfall.

TABLE (4) SULFATE-SULFUR CONTENT IN FRESH SNOW FROM AES WEATHER STATIONS 1973-74 (mg/l) [from March, 1975 Interim Report]

Athabasca	Banff	Beaverlodge	Brooks	Calgary	Cold Lake	Coronation	Drumheller	Edmonton	Edson
Dec. 8 0.0		Dec. 6 0.2 Dec. 11 0.3		Dec. 11 0.4		Dec. 12 0.1	Dec. 11 0.1		Dec. 11 0.0
Jan. 13 0.1	Jan. 12 0.1 Jan. 28 0.1	Jan. 12 0.0 Jan. 14 0.1 Jan. 27 0.0 Jan. 28 0.1	Jan. 26 0.6 Jan. 29 0.2	Jan. 3 1.0 Jan. 25 3.5 Jan. 28 0.6	Jan. 1 0.4 Jan. 14 0.3 Jan. 23 0.2	Jan. 2 0.4 Jan. 25 0.1 Jan. 30 0.1		Jan. 13 0.3 Jan. 27 0.5	Jan. 3 0.6 Jan. 12 0.3 Jan. 22 0.0 Jan. 27 0.0
	Feb. 28 0.1	Feb. 1 0.1 Feb. 3 0.1			Feb. 5 0.3 Feb. 11 0.2	Feb. 27 0.2			Feb. 2 0.3 Feb. 26 0.6
	Mar. 5 0.2	Mar. 12 0.2 Mar. 12 0.3 Mar. 16 0.2 Mar. 24 0.3	Mar. 5 0.3 Mar. 17 0.3	Mar. 5 0.4 Mar. 5 0.1	Mar. 1 0.4 Mar. 5 0.3	Mar. 2 0.5 Mar. 13 0.5		Mar. 17 0.2 Mar. 17 0.2	Mar. 4 0.2 Mar. 12 0.3 Mar. 21 0.2 Mar. 24 0.3 Apr. 1 0.3
Fairview	Ft. McMurray	Ft. St. John B.C.	Ft. Smith N.W.T.	Ft. Vermillion	Grande Prairie	Jasper	Lacombe	Lethbridge	Medicine Hat
Dec. 15 0.0 Dec. 16 0.0	Dec. 9 0.5 Dec. 28 0.2	Dec. 15 0.2	Dec. 24 3.8 Dec. 31 2.8		Dec. 12 0.1	Dec. 15 0.2	Dec. 3 0.3		Dec. 14 4.5 Dec. 17 22.5
Jan. 27 0.1 Jan. 28 0.1	Jan. 15 0.1	Jan. 14 0.0 Jan. 28 0.1	Jan. 10 0.2 Jan. 17 0.2	Jan. 20 0.6 Jan. 29 0.2	Jan. 6 0.0 Jan. 13 0.1 Jan. 22 0.1 Jan. 28 0.0	Jan. 16 0.2	Jan. 14 0.3 Jan. 22 0.1 Jan. 25 0.1	Jan. 7 0.2	Jan. 31 0.3
Feb. 28 0.2	Feb. 22 0.9	Feb. 25 0.6 Feb. 28 0.3		Feb. 12 0.2 Feb. 25 0.2	Feb. 1 0.1	Feb. 27 0.2 Feb. 27 0.2	Feb. 12 0.2		Feb. 27 0.3
Mar. 5 0.2 Mar. 14 2.8	Mar. 1 0.2	Mar. 16 0.1 Mar. 24 0.6	Mar. 19 0.1 Mar. 31 0.3 Mar. 31 0.2	Mar. 3 0.3 Mar. 11 0.2 Mar. 13 0.5	Mar. 9 0.1 Mar. 11 0.3 Mar. 13 0.5	Mar. 16 0.4	Mar. 17 0.2 Mar. 24 0.3		Mar. 13 0.1 Mar. 14 0.6 Mar. 14 0.3 Mar. 26 0.3 Mar. 26 0.5
Apr. 6 0.1 Apr. 12 0.4	Apr. 2 0.6								
Peace River	Pincher Creek	Ralston	Rocky Mountain House	Slave Lake	Vegreville				
Dec. 10 0.4	Dec. 17 0.4 Dec. 27 0.4		Dec. 27 0.1		Dec. 27 0.2				
Jan. 5 0.0 Jan. 14 0.3	Jan. 14 0.0 Jan. 29 0.4	Jan. 29 0.3	Jan. 3 0.2 Jan. 13 0.1 Jan. 20 0.3 Jan. 25 0.2 Jan. 28 0.0	Jan. 14 0.1 Jan. 15 0.4 Jan. 23 0.1	Jan. 13 0.1 Jan. 23 0.0 Jan. 27 0.2				
Feb. 25 0.1 Feb. 28 0.3	Feb. 20 0.3 Feb. 22 0.2	Feb. 27 0.1	Feb. 26 0.2	Feb. 11 0.2	Feb. 3 0.2 Feb. 11 0.3 Feb. 27 0.3				
Mar. 4 0.4 Mar. 16 0.2	Mar. 5 0.4		Mar. 5 0.3 Mar. 17 0.6 Mar. 23 0.5	Mar. 4 0.3	Mar. 4 0.3 Mar. 12 0.2 Mar. 18 0.6 Mar. 21 0.2 Apr. 30 1.1				

TABLE (5)

SULFATE-SULFUR CONTENT IN FRESH SNOW FROM AES WEATHER STATIONS 1974-75 (mg/l)

Athabasca	Banff	Beaverlodge	Brooks	Calgary	Cold Lake	Coronation	Drumheller	Edmonton
			Mar. 25 (1974) 0.6					
				Nov. 21 0.9	Nov. 18 0.0	Nov. 12 0.0	Nov. 21 0.0	
Dec. 24 0.2	Dec. 21 0.0 Dec. 21 0.0 Dec. 27 0.0	Dec. 21 0.0		Dec. 21 0.3		Dec. 22 0.1	Dec. 21 0.2	Dec. 22 0.0
Jan. 18 0.0		Jan. 27 0.0		Jan. 8 0.0 Jan. 20 1.2 Jan. 29 1.2	Jan. 6 0.0 Jan. 9 0.0 Jan. 23 0.0		Jan. 29 2.0	
	Feb. 12 0.05		Feb. 12 0.3	Feb. 2 0.2 Feb. 12 0.7		Feb. 3 0.2 Feb. 13 0.1	Feb. 3 0.3	Feb. 12 0.1
		Mar. 2 0.3 Mar. 4 0.7		Mar. 5 0.0	Mar. 5 0.2 Mar. 25 0.2	Mar. 24 0.8 Mar. 27 0.5	Mar. 8 0.2 Mar. 22 0.2	
			Apr. 7 0.1				Apr. 4 0.4 Apr. 8 0.2	
Edson	Fairview	Ft. Chipewyan	Ft. McMurray	Ft. St. John B.C.	Ft. Smith N.W.T.	Ft. Vermilion	Grande Prairie	Jasper
				*Sep. 4 0.5		no date 0.0 no date 0.3		
Nov. 21 0.3	Nov. 21 0.0		Nov. 21 0.4	Nov. 17 0.0	Nov. 30 0.2			
	Dec. 3 0.1			Dec. 16 0.0				
Jan. 7 0.2 Jan. 17 5.2	Jan. 23 0.4	Jan. 22 0.0 (A.P.) Jan. 22 0.1 (CdQP)	Jan. 17 3.2 Jan. 20 2.1	Jan. 6 0.1 Jan. 12 0.1 Jan. 23 0.0	Jan. 22 0.0	Jan. 19 0.0	Jan. 24 0.1 Jan. 27 0.0	Jan. 17 0.4
Feb. 10 0.8					Feb. 14 0.1			Feb. 12 0.2 Feb. 23 0.2
Mar. 3 0.4 Mar. 6 4.7	Mar. 3 0.0			Mar. 2 1.0 Mar. 17 0.5		Mar. 4 0.0	Mar. 24 0.1	Mar. 19 0.05
Apr. 3 0.8 Apr. 4 1.1				* rain			Apr. 13 1.2	
Lacombe	Medicine Hat	Peace River	Pincher Creek	Ralston	Rocky Mtn. House	Slave Lake	Vegreville	
					Oct. 5 0.1			
		Nov. 19 0.2				Nov. 18 0.0	Nov. 18 22.0	
	Dec. 22 0.5	Dec. 3 0.2	Dec. 12 0.0				Dec. 21 0.6	
Jan. 6 0.0	Jan. 4 0.2	Jan. 23 0.0	Jan. 25 0.0			Jan. 23 0.0 Jan. 28 0.2	Jan. 1 1.1 Jan. 12 0.1 Jan. 23 3.7 Jan. 31 1.9	
Feb. 2 0.0 Feb. 9 0.1 Feb. 23 0.2	Feb. 9 0.1		Feb. 2 0.4 Feb. 7 0.2 Feb. 11 0.1	Feb. 10 0.1				
Mar. 23 0.4	Mar. 23 0.2	Mar. 3 0.05		Mar. 25 0.2 Mar. 26 0.1		Mar. 3 0.2	Mar. 2 1.5 Mar. 17 5.2 Mar. 26 2.8 Mar. 29 1.2	
Apr. 2 0.5	Apr. 4 0.2 Apr. 6 0.4			Apr. 1 0.2			Apr. 5 1.9 Apr. 8 1.9 Apr. 9 8.5 Apr. 27 3.0	

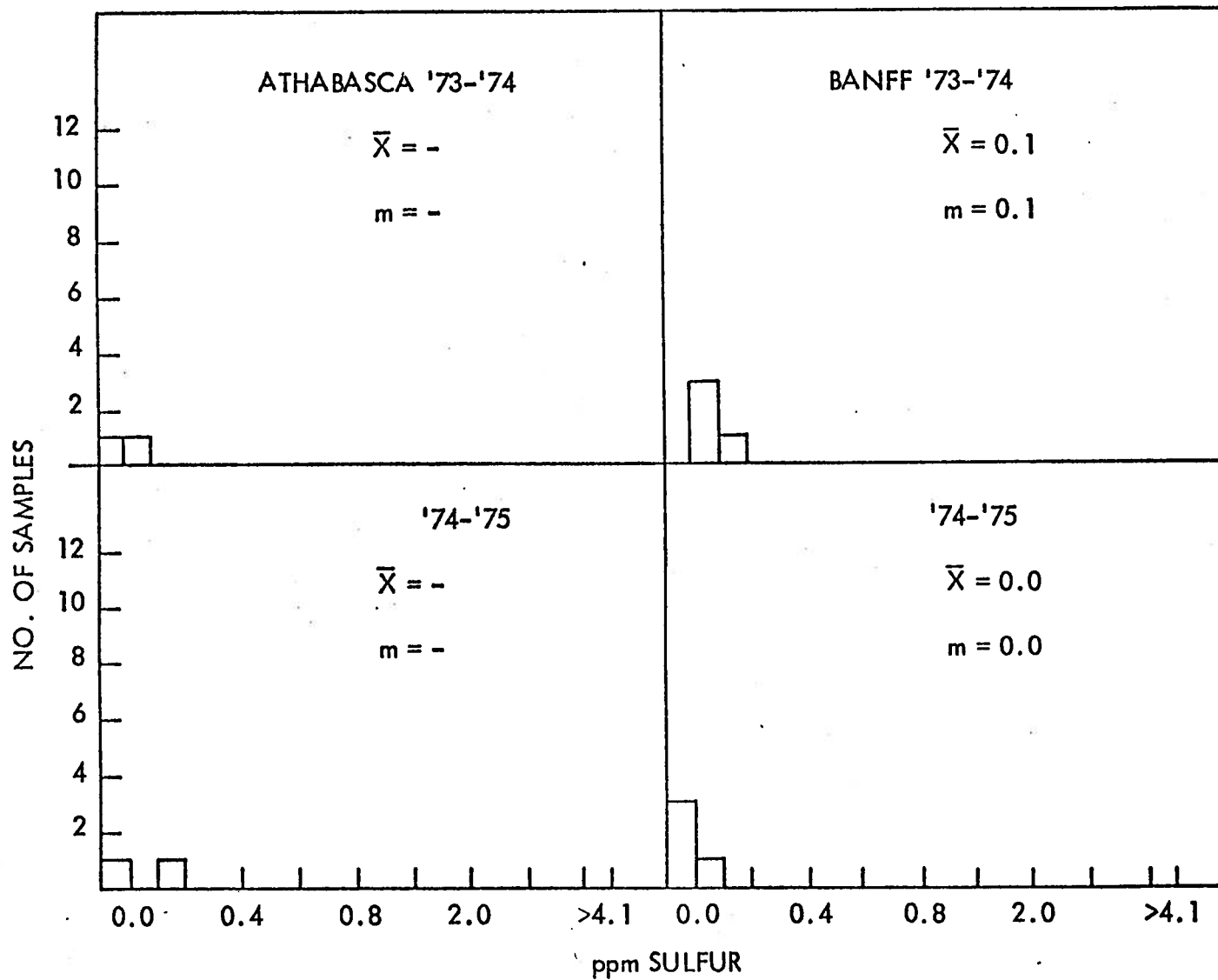


Figure 40: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

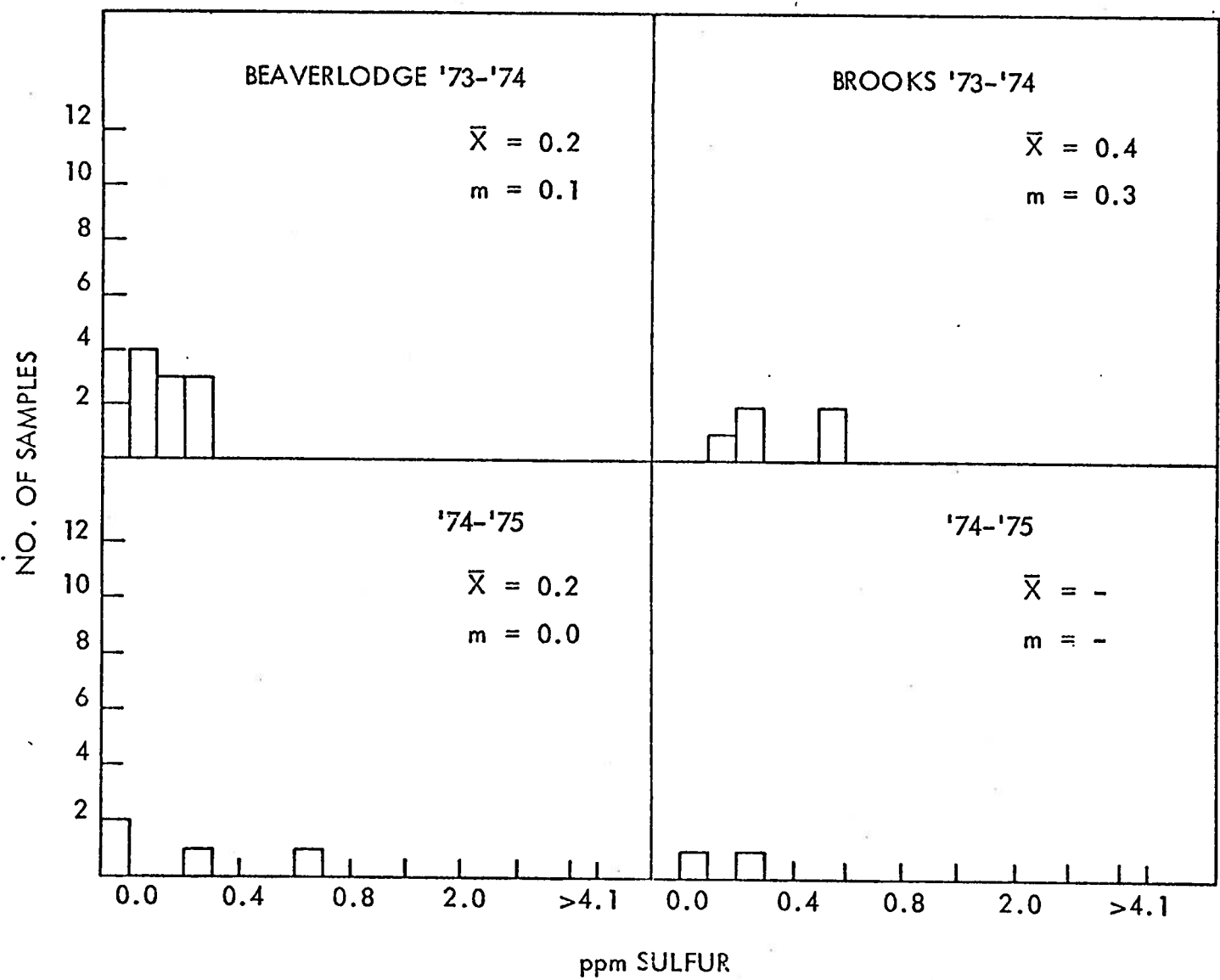


Figure 41: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

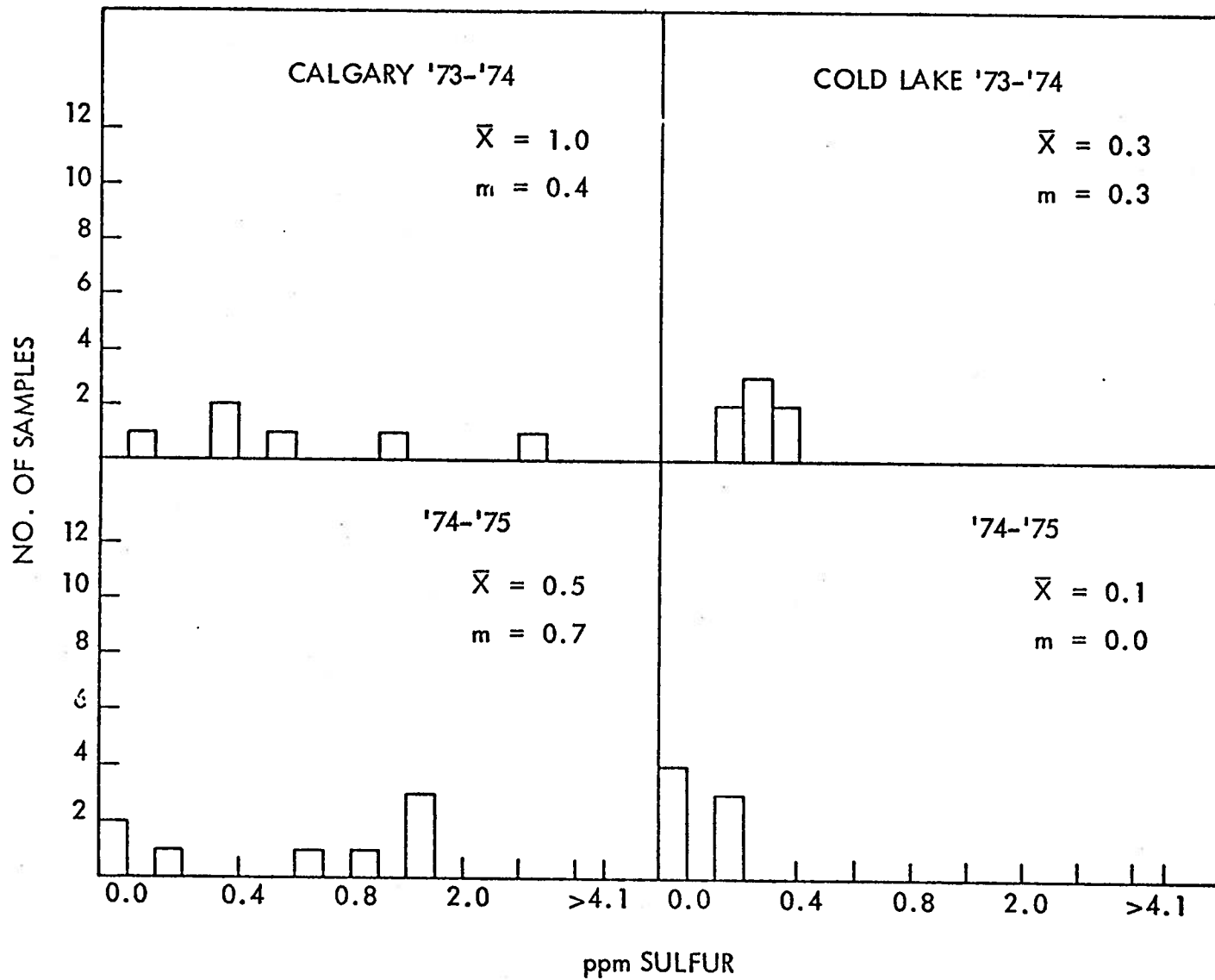


Figure 42: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

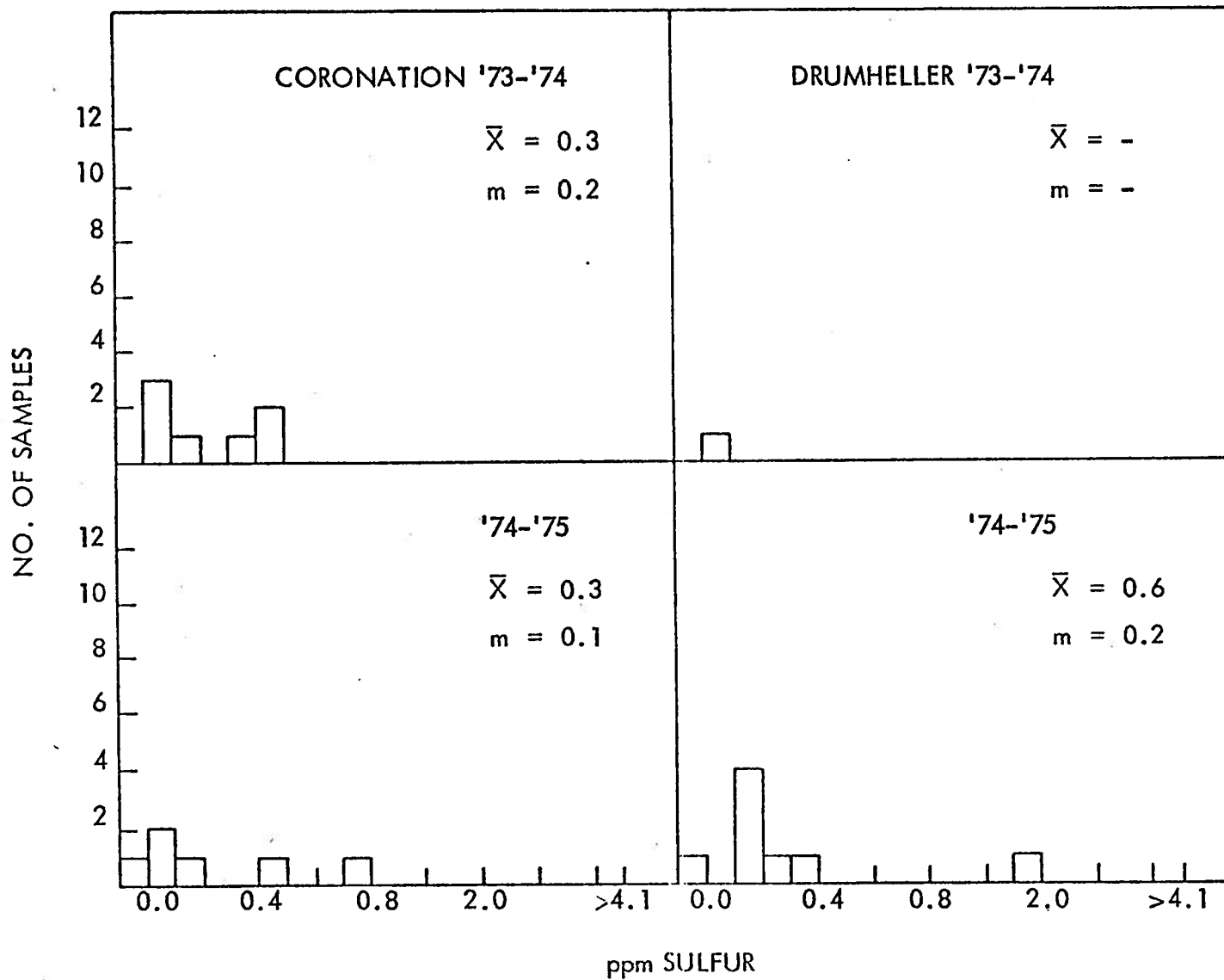


Figure 43: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

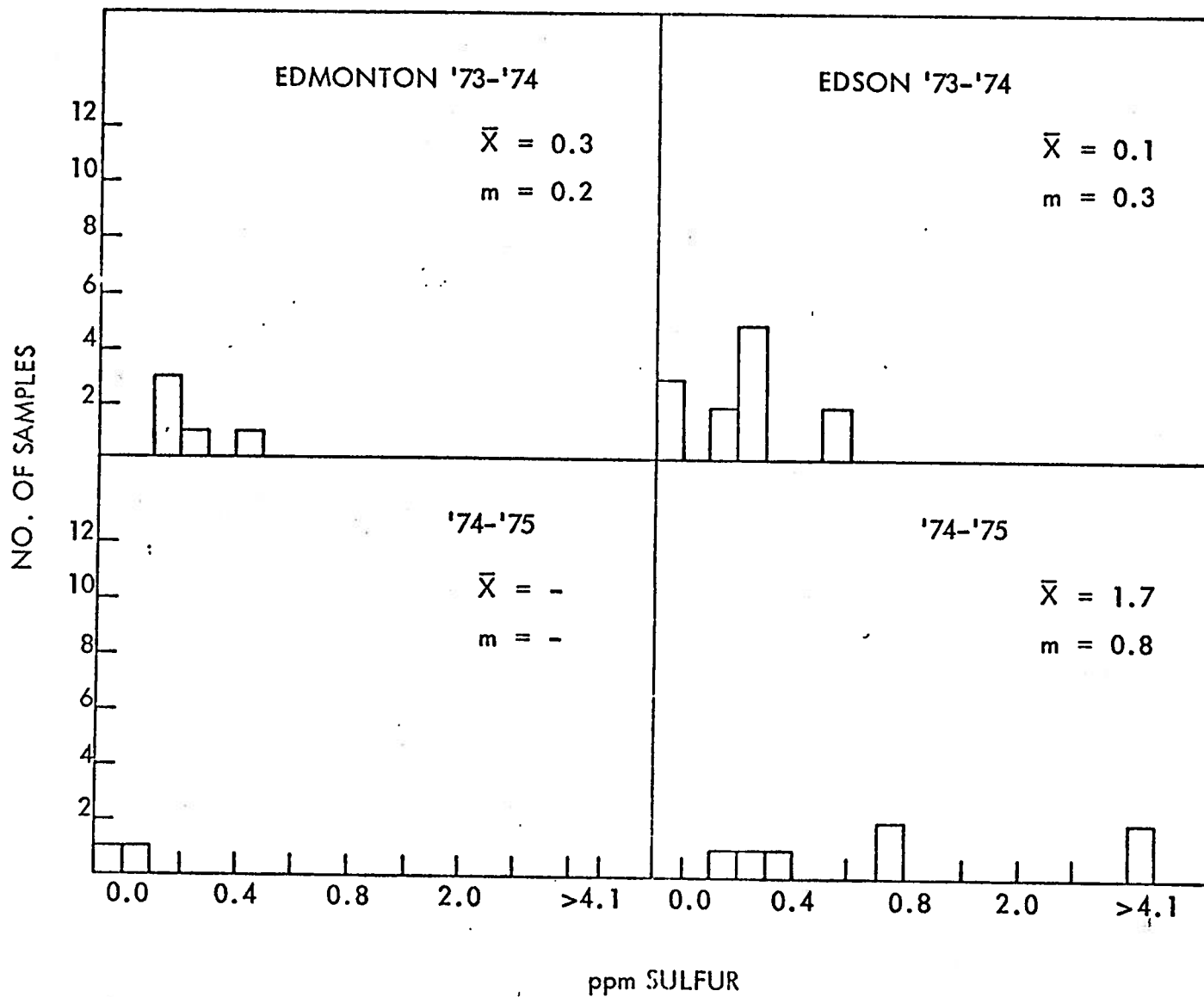


Figure 44: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

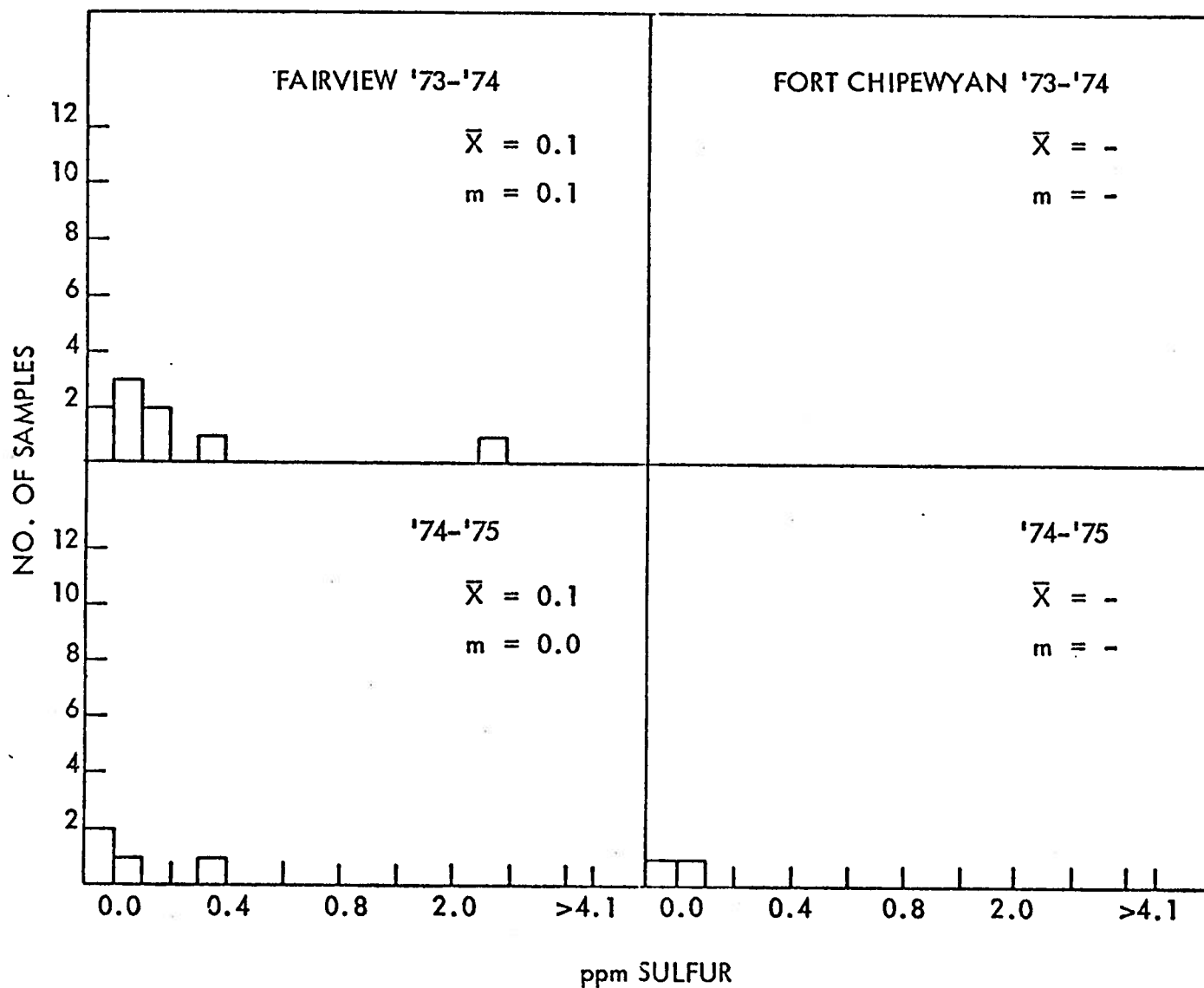


Figure 45: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

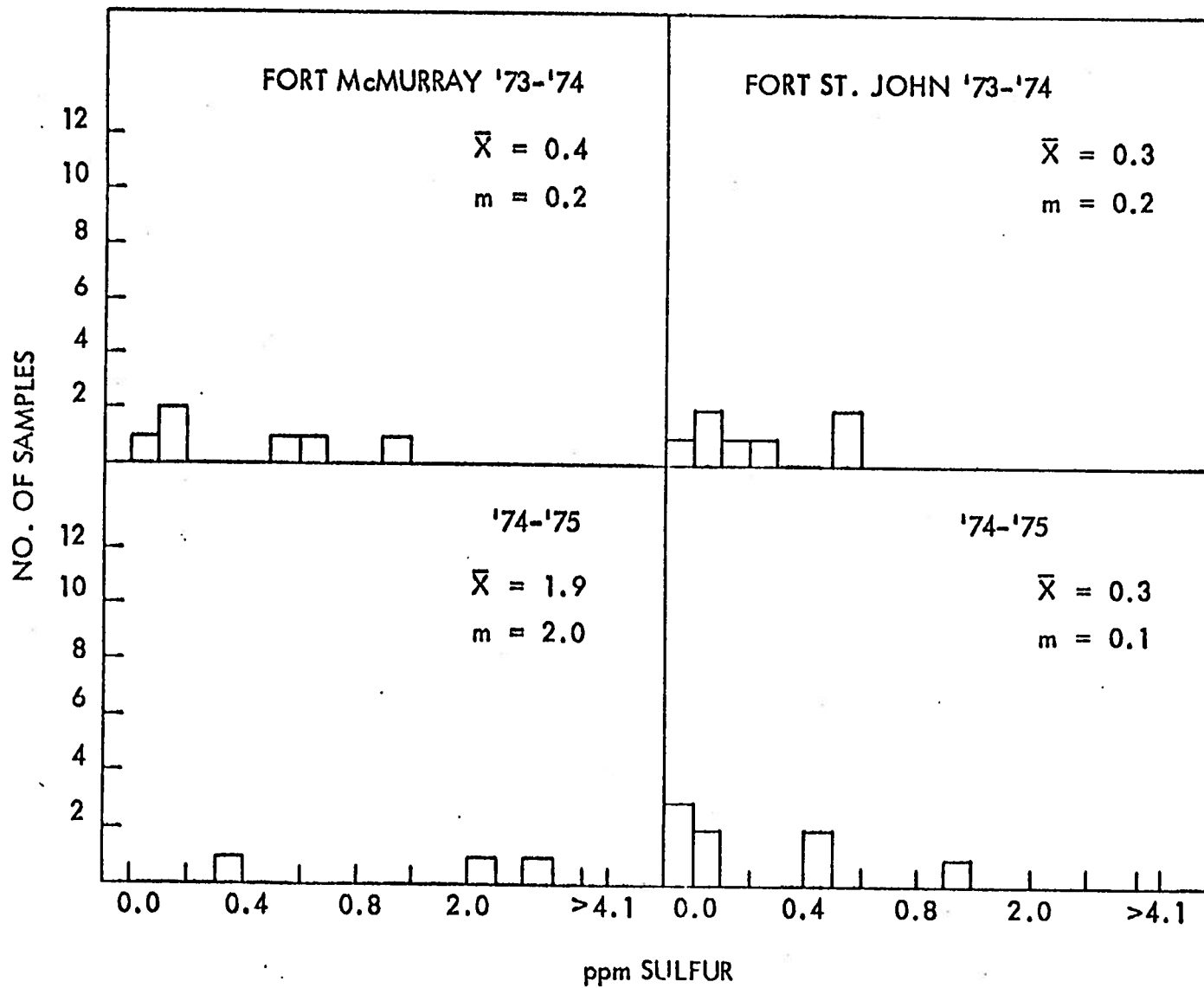


Figure 46: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

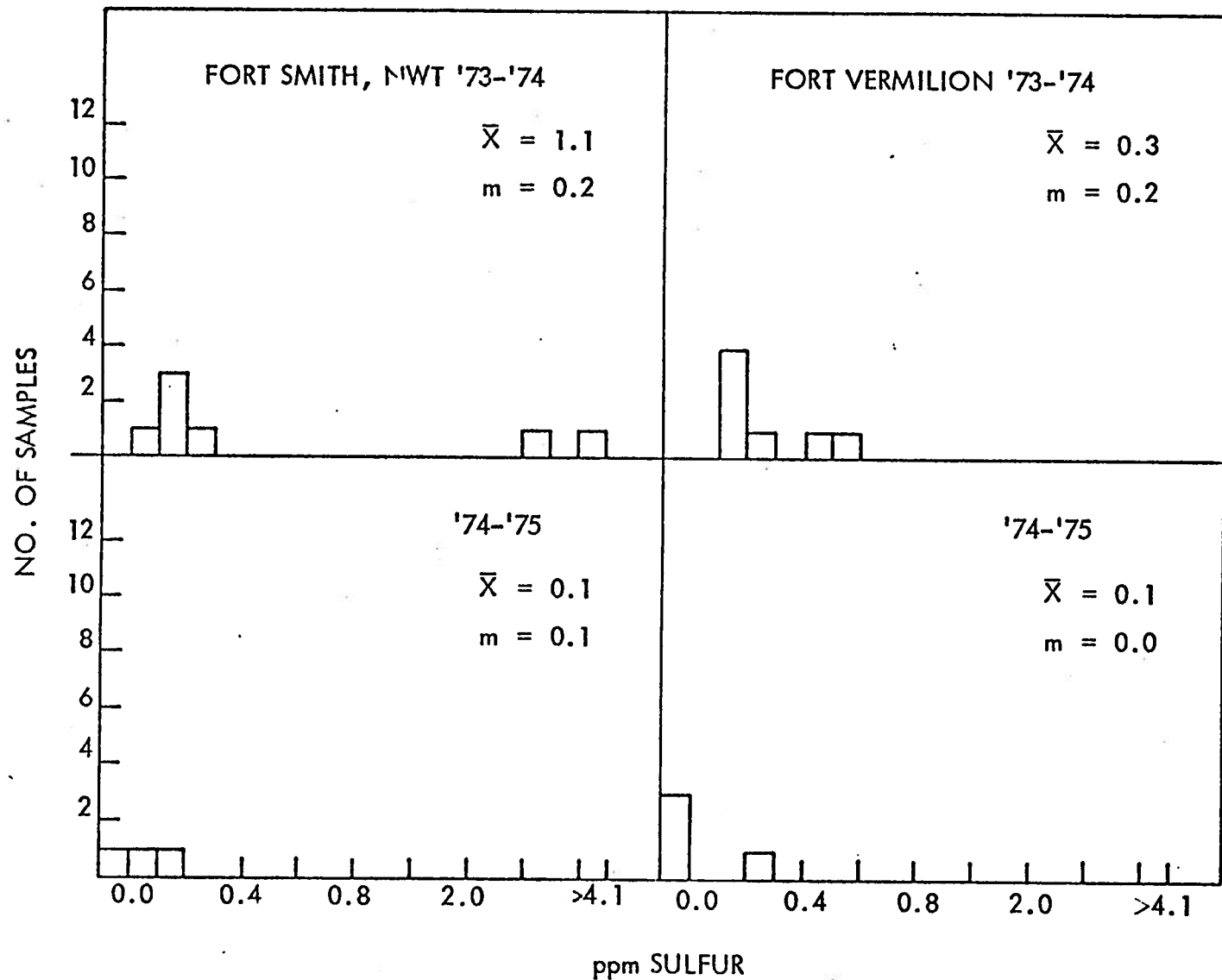


Figure 47: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

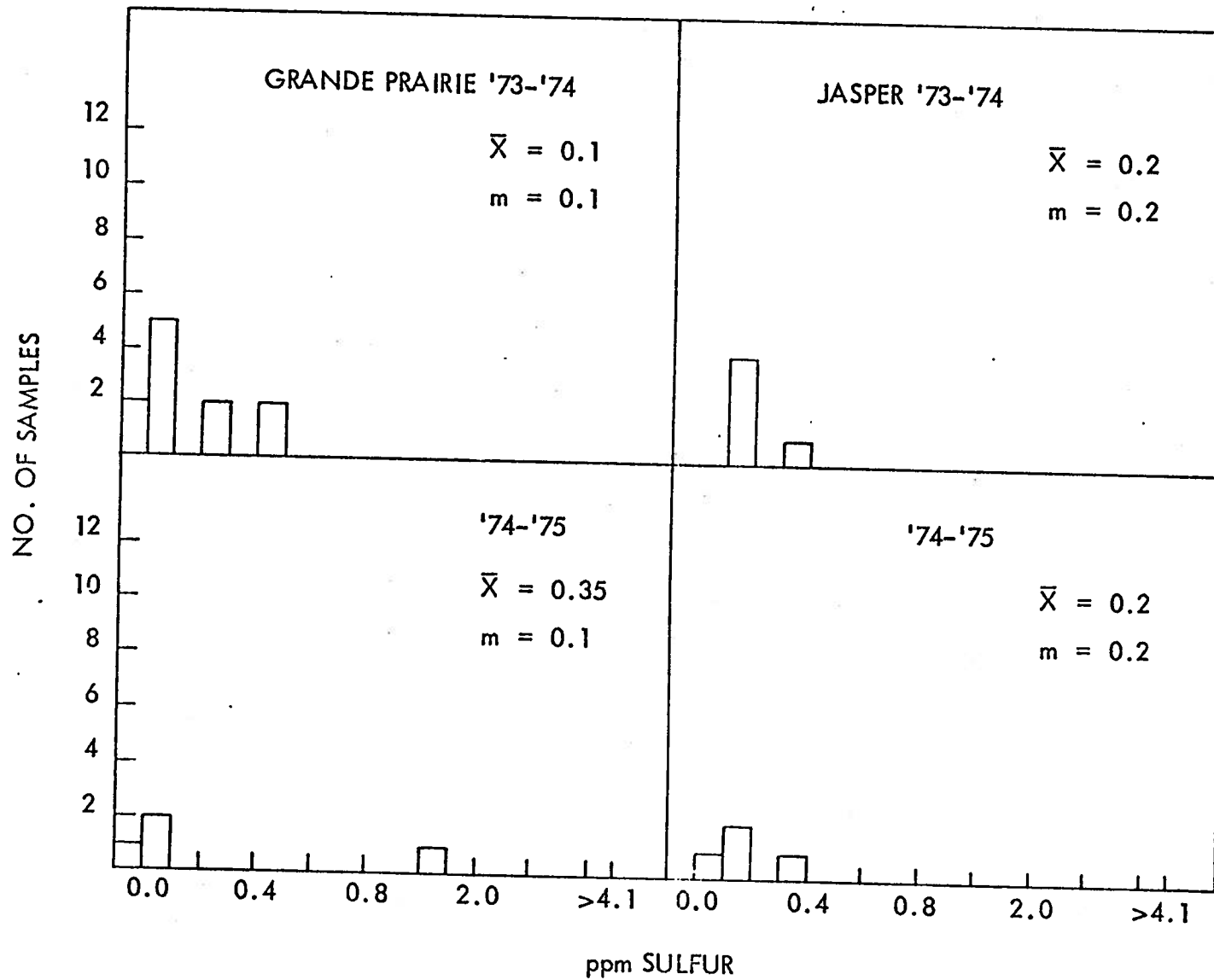


Figure 48: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

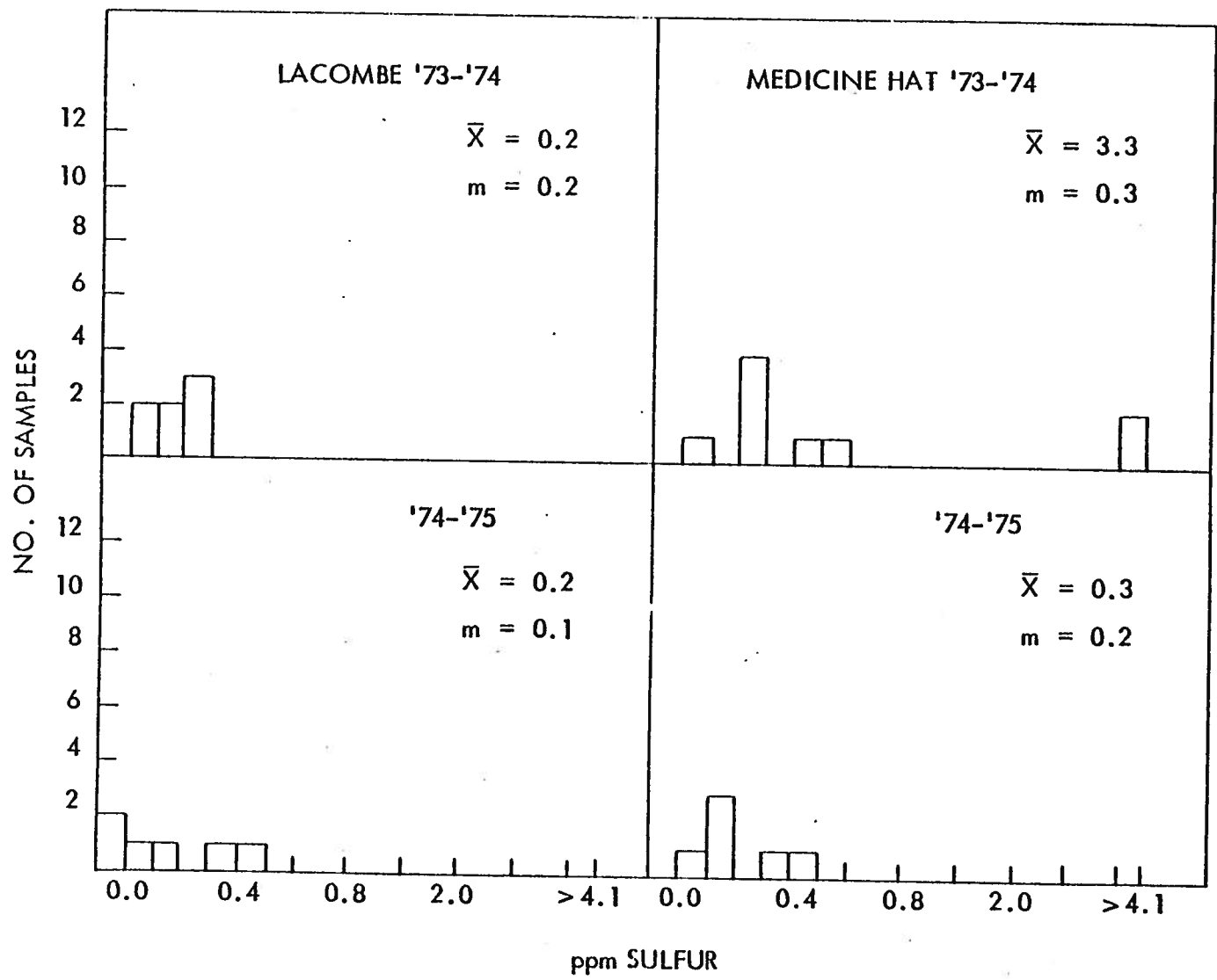


Figure 49: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

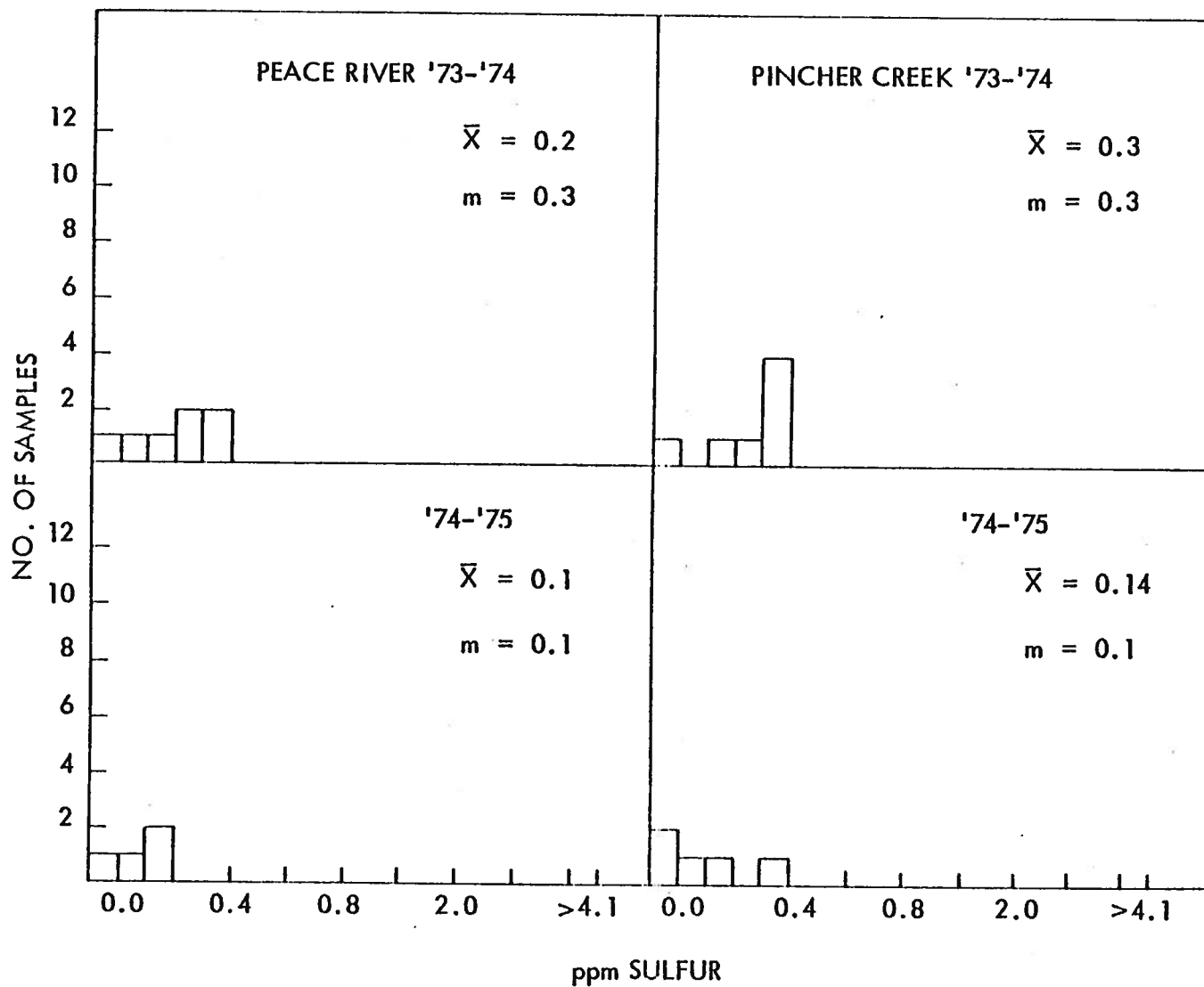


Figure 50: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value
 m = median value

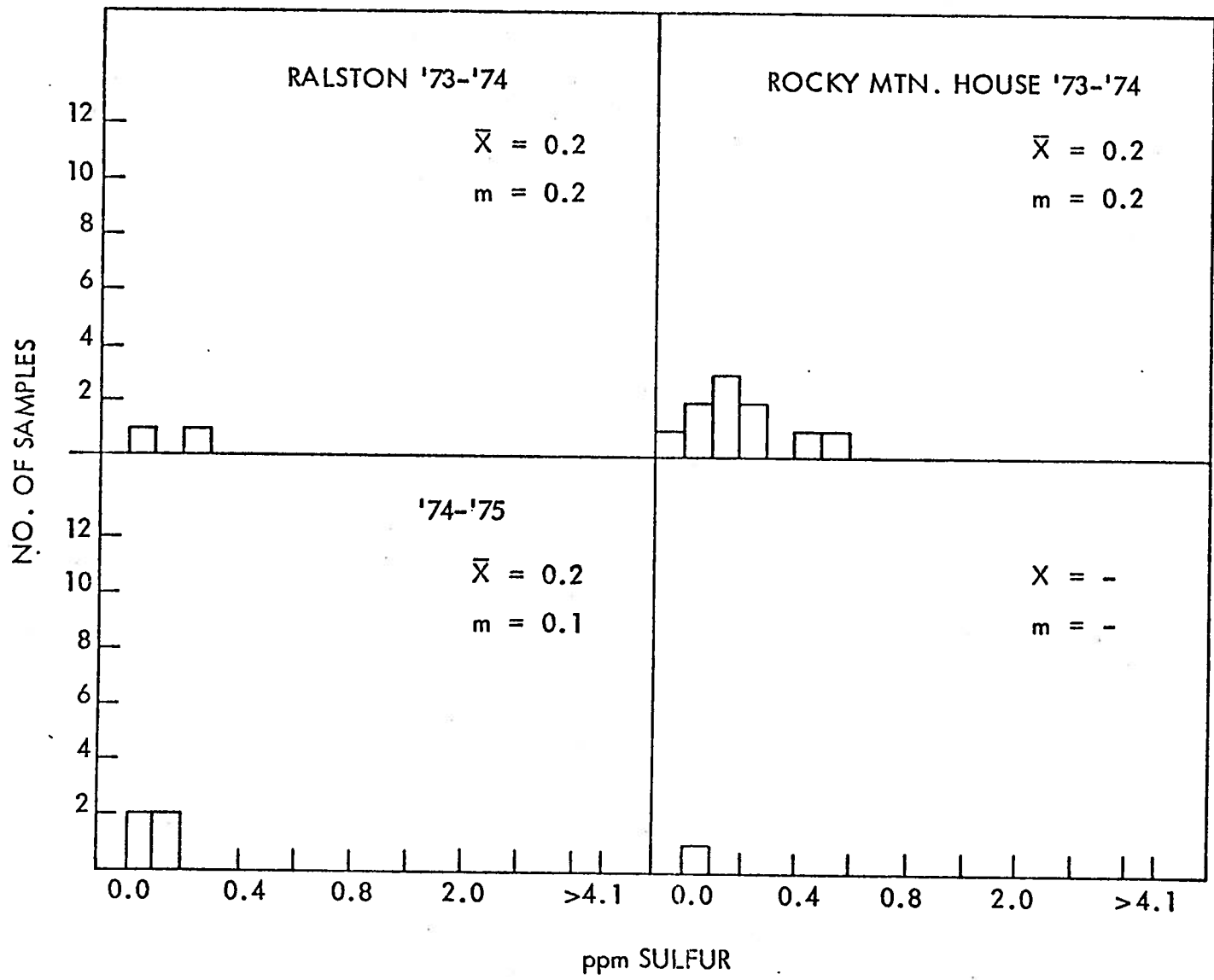


Figure 51: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.
 \bar{X} = average value
 m = median value

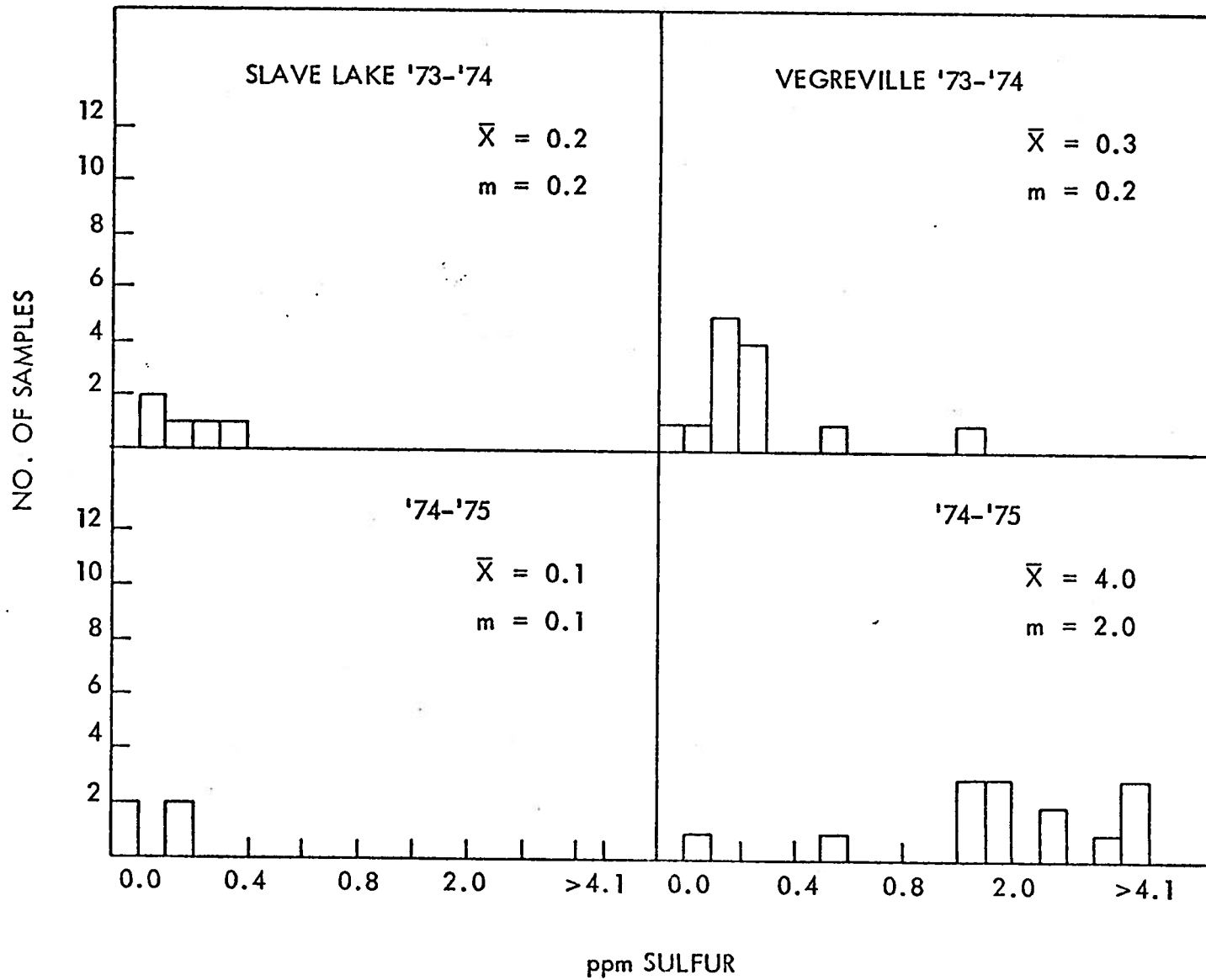


Figure 52: Range of SO_4-S values (ppm) for all snowfall events at the indicated location.

\bar{X} = average value

TABLE (6)

Concentration of sulfate-sulfur in mg/l for total depth
of snow and corresponding calculated lbs sulfate-sulfur/acre, 1974

Dates: February 13-16, 1974

Sample	Location	Snow Depth	Sulfate-sulfur mg/l	Sulfur/acre lbs
SN 1	Texaco Gas Plant, Bonny Glen SW 17-47-27- W4	33 1/2	0.6	0.9
SN 2	Pigeon Lake (Mulhurst) SW 13-47- 1- W5	2 x 15	0.3	0.3
SN 3	Mission Beach LDS 6-25-47- W5	28	0.3	0.3
SN 4	Pigeon Lake SW 23-48- 1- W5	3 x 11 1/2	0.3	0.3
SN 5	Glen Park NW 32-48-27- W4	26	0.4	0.3
SN 6	Wetaskiwin SW 16-46-24- W4	2 x 24.2	0.4	0.5
SN 7	Wetaskiwin SE 13-46-26- W4	2 x 20 1/2	0.5	0.5
SN 8	Usona SW 1-45-26- W4	2 x 23	0.4	0.4
SN 9	Usona SE 5-45-27- W4	2 x 22 1/2	0.2	0.2
SN 10	Falun NW 10-46-27- W4	2 x 21	0.3	0.3
SN 11	Amoco Battery LSD 10-24-46-28- W4	26.0	0.2	0.2
SN 12	Mameo Beach NW 14-46-28- W4	32.0	0.6	1.2
SN 13	Yeoford SW 31-46- 2- W5	28	0.2	0.2
SN 14	Norbuck SW 2-47- 4- W5	25	0.3	0.4
SN 15	Winfield SW 12-46- 3- W5	21 1/2	0.2	0.4
SN 16	Hoadley SE 4-45- 3- W5	2 x 17.2	0.3	0.2

Table (6) - continued

Sample	Location	Snow Depth	Sulfate-sulfur Sulmg/1	Sulfur/acre lbs
SN 17	Hoadley SE 4-45- 2- W5	2 x 25 1/2	0.3	
SN 18	Bluffton SE 4-44- 2- W4	2 x 22	0.4	
SN 19	Rimbey SE 4-43- 2- W5	2 x 21	0.3	0.3
SN 20	Rimbey SE 3-43- 1- W5	2 x 30	0.2	
SN 21	Rimbey Gas Plant SE 23-43- 1- W5	24	0.2	
SN 22	Rimbey Gas Plant SE 24-44- 1- W5	26	0.3	
SN 23	Rimbey Gas Plant S 5-44- 1- W5	2 x 22	0.4	0.4
SN 24	Ponoka SW 7-43-25- W4	3 x 12	0.6	0.4
SN 25	Menaik NW 35-43-25- W4	2 x 17	0.4	0.4
SN 26	Hobbema SW 4-45-24- W4	25	0.4	0.7
SN 27	Hobbema NE 35-44-23- W5	2 x 25	0.3	
SN 28	New Norway NE 31-44-21- W4	24	0.5	0.5
SN 29	New Norway NW 7-45-21- W4	24	0.4	0.4
SN 30	Ferintosh NE 3-44-21- W4	2 x 17	0.3	0.2
SN 31	Bashaw SW 3-42-21- W4	2 x 16	0.6	0.4
SN 32	Bashaw SW 2-42-20- W4	28	0.4	0.5
SN 33	Donalda NE 6-42-18- W4	2 x 22	0.3	0.2

Table (6) - continued

Sample	Location	Snow Depth	Sulfate-sulfur mg/l	Sulfur/acre lbs
S 34	Redwillow SE 19-40-18- W4	2 x 16	0.4	0.6
S 35	Botha NW 33-38-18- W4	2 x 18	0.4	0.4
S 36	Stettler SE 5-39-19- W4		0.6	
S 37	Stettler NE 6-39-19- W4	2 x 13	1.4	1.1
SN 38	Erskine SE 1-39-21- W4	3 x 11	0.7	0.3
SN 39	Nevis SW 5-39-21- W4	20	0.3	
SN 40	Nevis Gas Plant NE 11-39-22- W4	21	0.8	0.6
SN 41	Nevis Gas Plant NE 10-39-22- W4	20	0.3	
SN 42	Nevis Gas Plant SW 23-39-22- W4	10	0.3	0.2
S 43	Mirror NW 21-40-22- W4	2 x 12	2.7	1.6
S 44	Tees SW 30-40-23- W4	2 x 24	0.4	0.4
S 45	Clive SE 12-40-25- W4	26	0.3	0.3
S 46	Lacombe SW 31-40-26- W4		0.8	1.4
S 47	CF Penhold NE 14-37-28- W4	16	0.6	0.5
SN 48	Sylvan Lake SW 4- 39-28- W4	22	0.9	1.4
SN 49	Sylvan Lake SE 28-39- 1- W5	2 x 20	1.1	0.7
SN 50	Bentley SE 17-41- 1- W5	20	0.4	0.4
SN 51	Gull Lake SE 26-40-28- W4	2 x 20	0.3	0.1

Table (6) - continued

Sample	Location	Snow Depth	Sulfate-sulfur mg/1	Sulfur/acre lbs
SN 62	Gull Lake NE 25-41-28- W4	22	0.3	0.2
SN 63	Ponoka NW 3-43-26- W4	2 x 16	0.4	0.4
SN 64	Ponoka NW 3-43-26- W4	2 x 14	0.4	0.4
SN 65	Ponoka SE 6-43-24- W4	27	0.4	0.6
SN 66	Leduc NE 25-49-25- W4	30	0.7	1.3

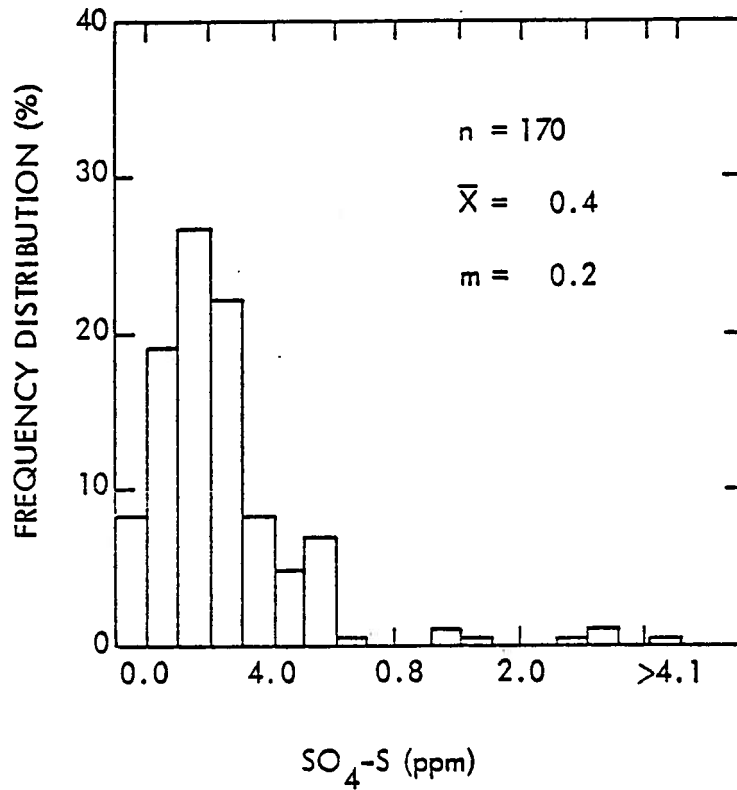


Figure 53: Frequency distribution (%) of SO₄-S in fresh snow obtained from AES weather stations, 1973-1974.

n = no. of samples analysed
 \bar{X} = average value
 m = median value

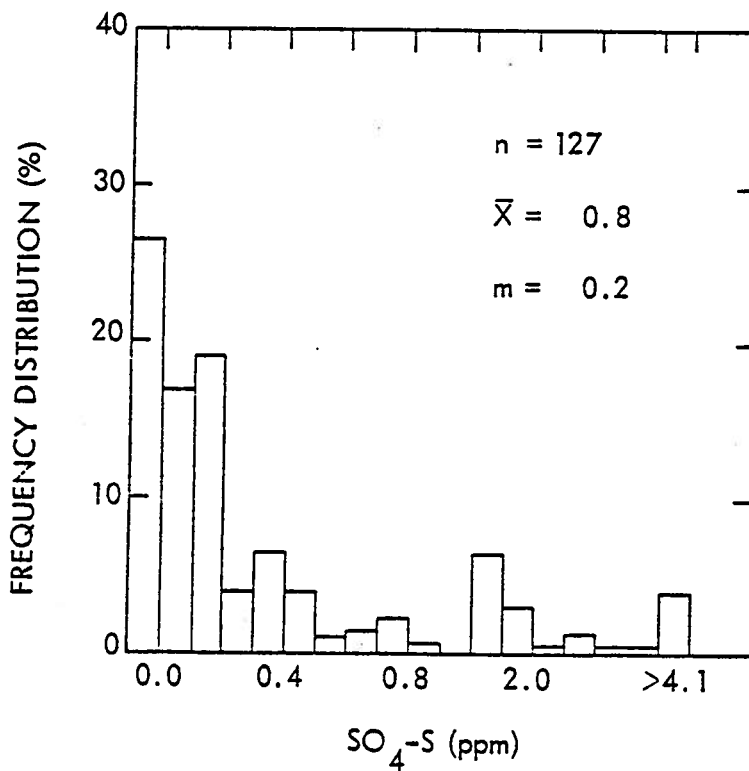


Figure 54: Frequency distribution (%) of SO₄-S in fresh snow obtained from AES weather stations, 1974-1975.

n = no. of samples analysed
 \bar{X} = average value
 m = median value

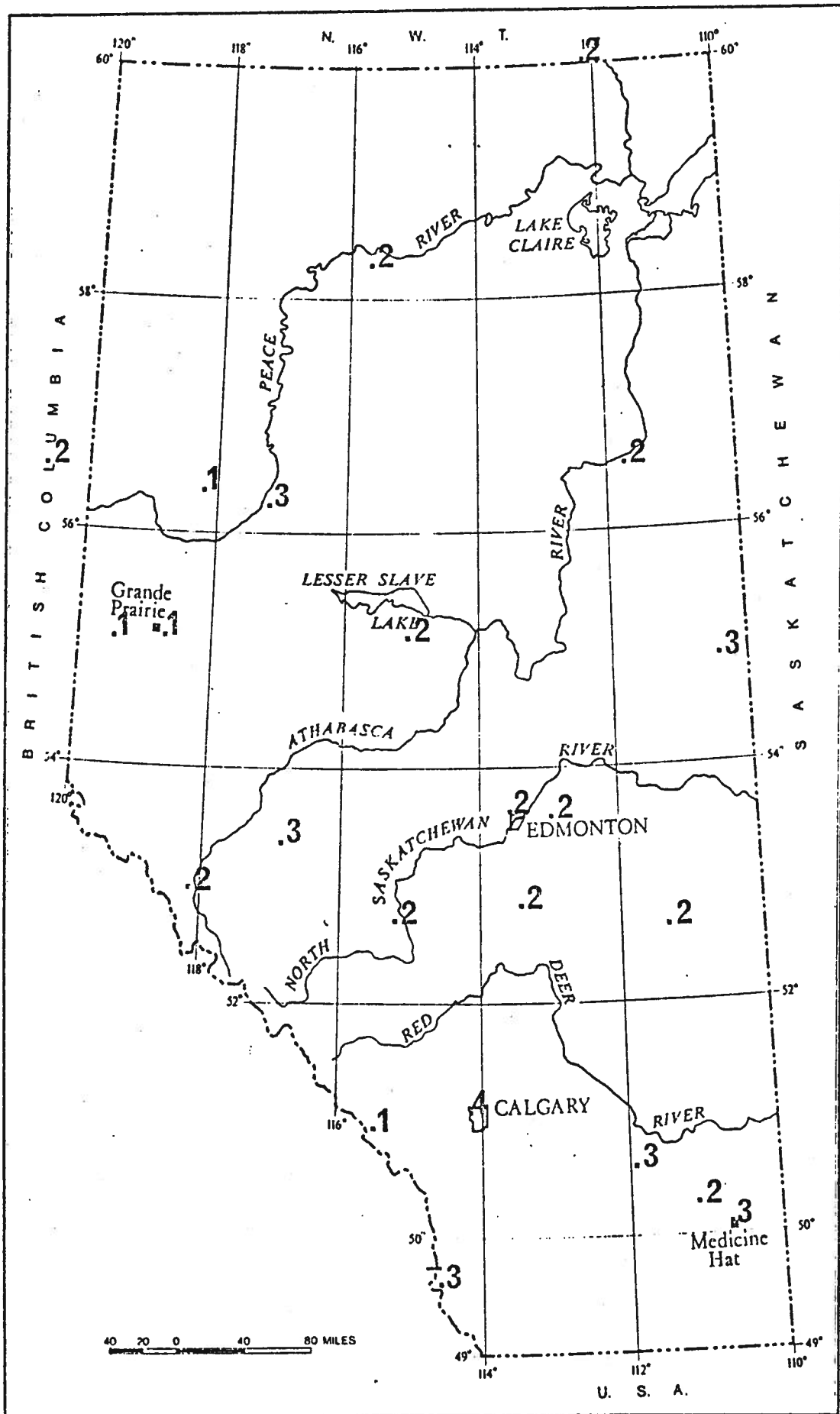


Figure 55: Median SO₂-S (ppm) in fresh snow obtained from AES weather stations, 1973-1974.

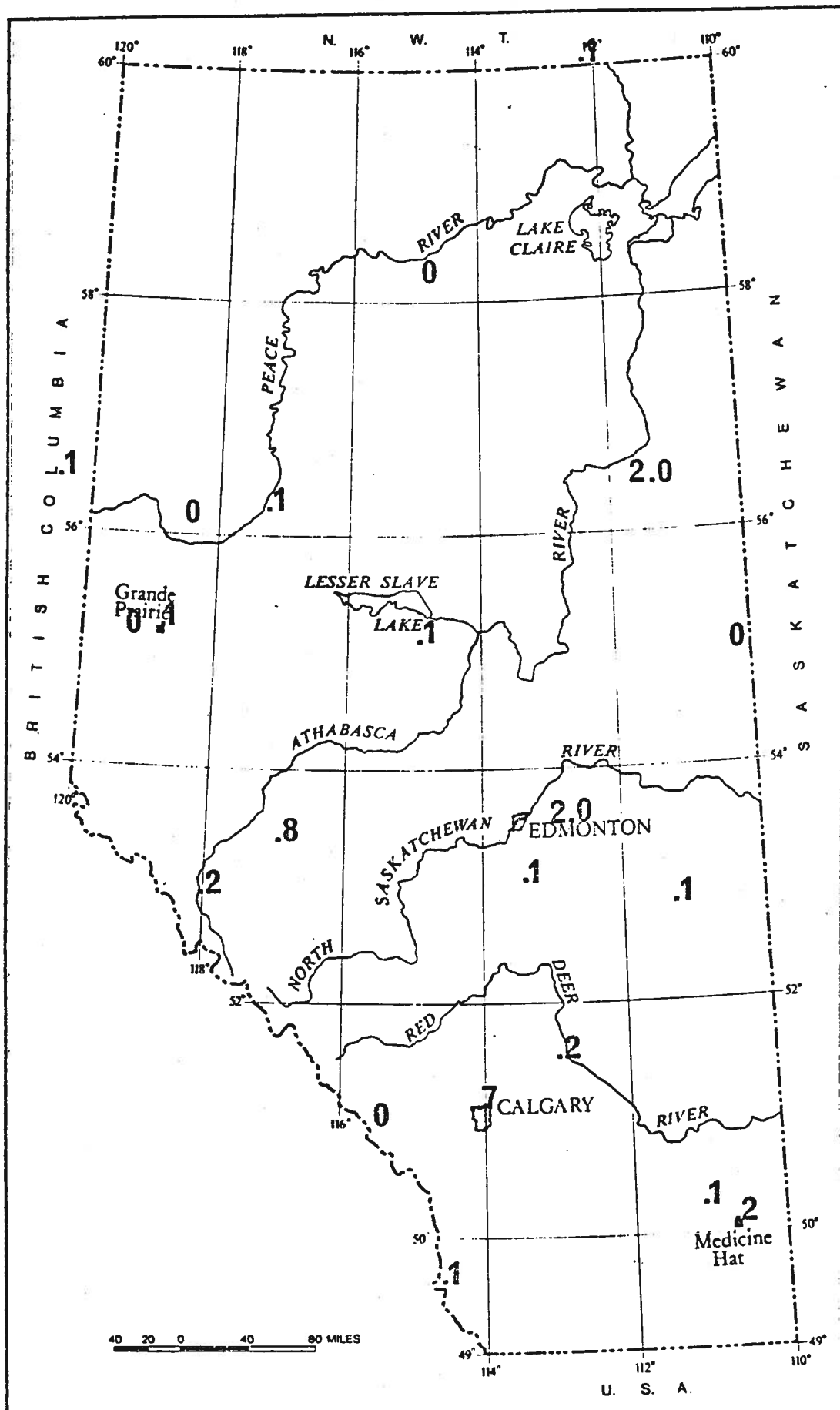
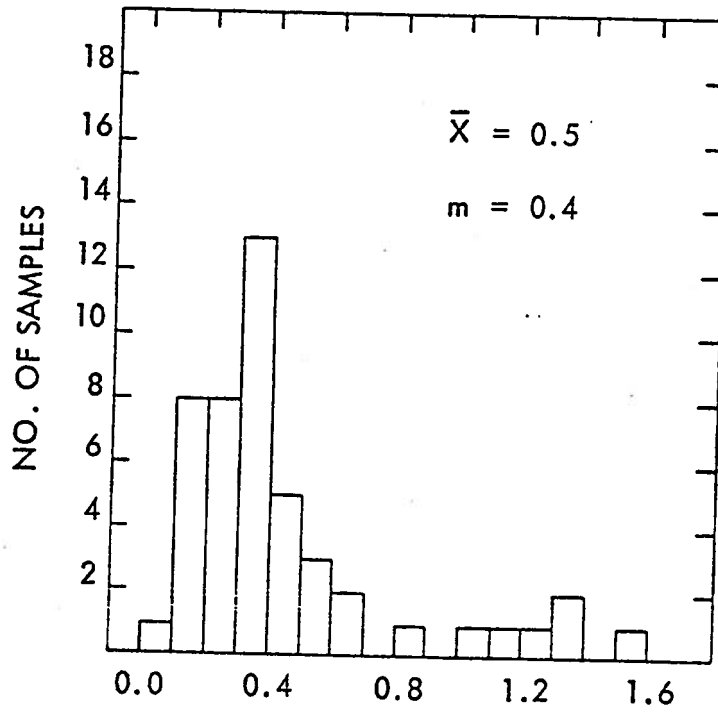


Figure 56: Median $\text{SO}_2\text{-S}$ (ppm) in fresh snow obtained from AES weather stations, 1974-1975.



LB/ACRE SO_4-S AS OBTAINED FROM
TOTAL DEPTH OF SNOW NOV. 1 '73 - FEB. 13 '74

Figure 57: Variability of SO_4-S content (lbs SO_4-S /acre) in total depth of snow; November 1, 1973 - February 13, 1974.

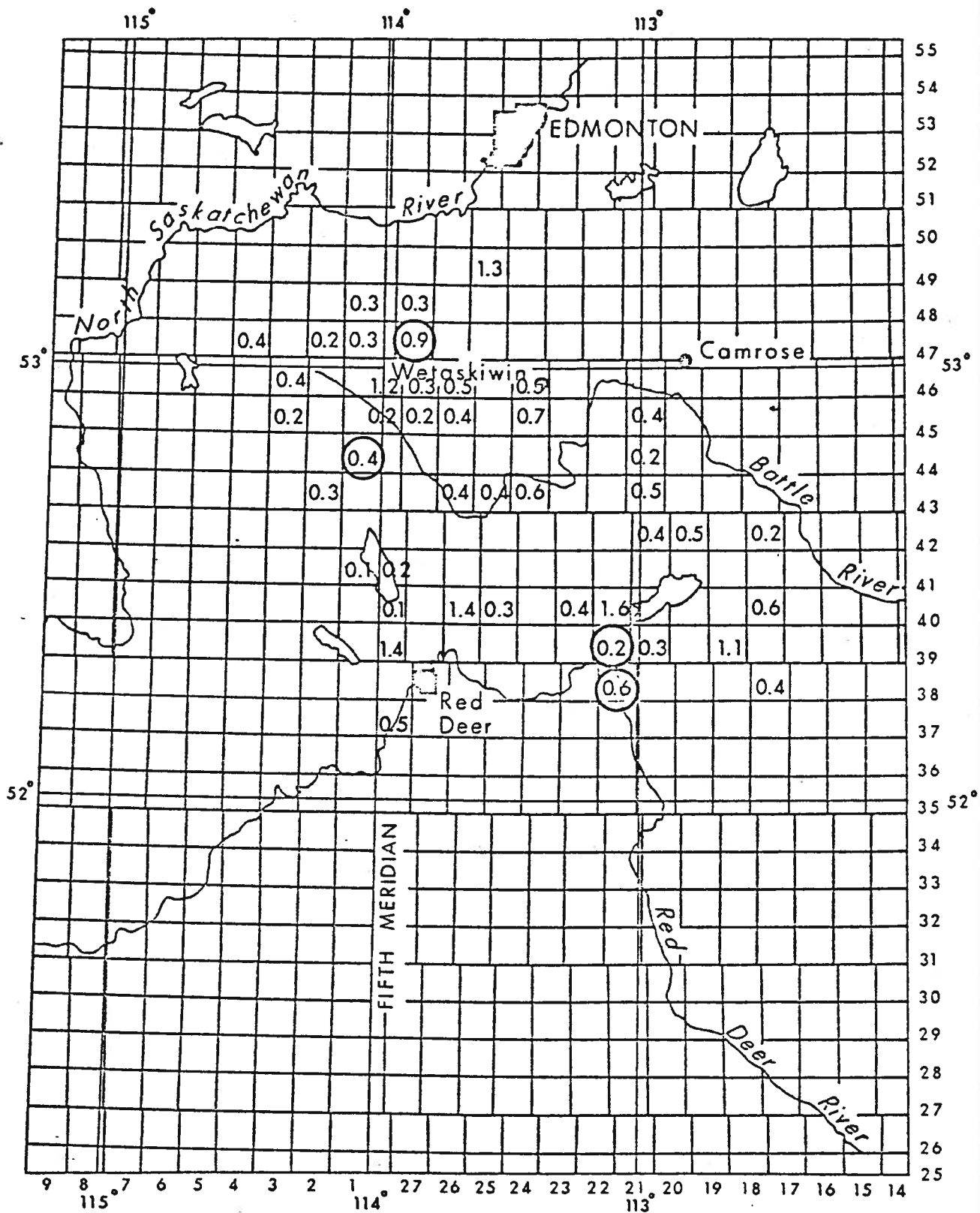


Figure 58: SO_4-S (lbs/acre) November 1st, 1973 - February 13th, 1974 in total depth of snow.

- 0.4 = Home Glen Rimbe
- 0.9 = Bonnie Glen
- 0.2 = Chevron Nevis
- 0.6 = Gulf Nevis

TABLE 9 Sulfate-sulfur (mg/l), pH and specific conductance (K)
for selected fresh snow samples from AES
Weather Stations, 1973-74

Date	S mg/l	pH	K (μ mho)	Date	S mg/l	pH	K (μ mho)
BANFF				CALGARY			
Mar. 5	0.2	7.3	---	Mar. 5	0.1	7.7	---
CORONATION				COLD LAKE			
Feb. 27	0.2	6.0	---	Feb. 11	0.2	5.6	---
Mar. 2	0.5	6.2	5.1				
Mar. 13	0.5	7.1	---				
EDMONTON				EDSON			
Mar. 17	0.2	5.7	4.9	Mar. 12	0.3	5.1	---
				Mar. 21	0.2	6.2	---
FAIRVIEW				FT. VERMILION			
Apr. 6	0.1	6.4	---	Mar. 11	0.2	5.8	---
Apr. 21	0.4	5.2	9.2				
LACOMBE				MEDICINE HAT			
Feb. 12	0.2	5.6	---	Mar. 26	0.3	7.1	---
				Mar. 26	0.5	7.4	---
ROCKY MOUNTAIN HOUSE				VEGREVILLE			
Mar. 17	0.3	4.8	10.5	Dec. 27	0.2	7.9	---
Mar. 23	0.5	5.0	---	Feb. 11	0.3	5.1	---
				Feb. 27	0.3	6.3	---

TABLE 10 pH and (Specific Conductance in μ hos) from dry fallout + rain samples submitted by AES Weather Stations. See Table (2) for associated sulfate-sulfur concentration

Athabasca	Banff	Calgary	Cold Lake	Coronation	Edmonton	Edson	Fairview	Ft. McMurray
May 24 7.7					May 23 6.8			
June 8 6.8	June 26 7.6 (45.9)	June 7 7.6		June 3 7.4 June 6 6.6 (25.8)	June 3 6.5 (7.4) June 22 (24.8)	June 6 7.7		June 6 6.4
July 3 7.1		July 1 6.4 (133.3)		July 8 6.4				July 9 6.4
July 9 6.5 July 9 7.3			July 24 6.8 (14.9) July 30 7.1					July 25 6.4
July 11 7.1* July 12 6.3 (11.4)			Aug. 6 6.4 (6.4)	Aug. 10 7.4				
	Aug. 11 7.2 (17.9)	Aug. 10 6.4 (49.5)				Aug. 11 6.8	Aug. 18 6.7	Aug. 17 7.4
Aug. 23 5.4 (8.1)	Aug. 13 7.3	Aug. 19 6.3	Aug. 16 7.1			Aug. 19 5.9	Aug. 23 7.7	
	Sept. 10 7.0		Sept. 6 6.4 Sept. 10 6.9			Sept. 5 6.9	Sept. 4 7.1	
*Hail								
Ft. St. John B.C.	Ft. Smith N.W.T.	Grande Prairie	Jasper	Lacombe	Medicine Hat	Pincher Creek	Peace River	Rocky Mtn. House
May 26 6.4		May 23 6.8	May 27 6.7		May 31 7.6	May 30 6.9		
June 26 7.1	June 13 6.5		June 6 6.7 June 22 6.9 June 30 (20.7)	June 4 6.4 June 6 6.5 (22.7)			June 27 6.3	
July 10 5.0	July 2 6.7 July 7 6.7 July 16 5.0	July 30 7.7		July 5 6.4 July 22 5.9			July 1 7.2 July 2 5.6 (5.0)	July 8 7.4
Aug. 18 6.8	Aug. 8 6.7 Aug. 18 7.3		Aug. 10 8.3	Aug. 6 6.3	Aug. 13 7.2	Aug. 8 7.1 Aug. 10 7.1 Aug. 12 6.9	Aug. 20 6.5	Aug. 9 6.7 Aug. 11 6.2 Aug. 18 6.2 (5.4)
	Sept. 4 7.0		Aug. 23 6.4			Aug. 29 7.7 Aug. 31 6.8	Aug. 23 6.1 Aug. 27 6.4	Aug. 22 7.2
						Sept. 10 6.9 (29.4)		Sept. 27 7.4 Sept. 29 7.7
			Oct. 1 6.5 Oct. 16 6.6					
Slave Lake	Vegreville							
	May 24 6.2							
	June 4 6.6 June 4 6.5 June 8 6.5 June 26 7.5							
July 11 6.2 (2.1)								
July 30 5.4 (5.7)								
	Aug. 7 6.3 Aug. 14 6.9 Aug. 17 6.5							
Sept. 9 6.9	Sept. 9 6.5 Sept. 10 6.8							

TABLE 12 Sulfur uptake under controlled atmosphere:
60 ppb SO₂ and 38 ppb SO₂

Material exposed to SO ₂		10 days 60 ppb SO ₂			10 days 38 ppb SO ₂		
		SO ₄ - S ppm			SO ₄ - S ppm		
		Exposed	Control	Gain	Exposed	Control	Gain
Flater	dry	11.4	4.8	6.6	10.6	4.4	6.2
	wet	12.3	5.4	6.9	12.2	5.1	7.1
Stewart	dry	10.5	3.9	6.6	9.6	4.7	4.9
	wet	11.7	4.2	7.5	10.8	5.5	5.3
Stewart +CaCO ₃	dry				18.5	13.9	5.4
	wet				18.4	15.4	3.0
Bark	78	78.0	48	30	64	41	26.0
Breton	dry	18.9	7.2	11.7			
	wet	18.5	8.4	10.1			
Ellerslie	dry	15.9	7.0	8.9			
	wet	18.0	6.8	11.2			
H ₂ O		1.4	0.0	1.4	1.95	0.10	1.85

TABLE 13 Summary: Rate of Sulfur Uptake under controlled atmospheres

		10 day run, 60 ppb SO ₂			10 day run, 30 ppb SO ₂			30 day run, 24 ppb SO ₂		
		Gain SO ₄ -S ppm lbs/acre	Rate* lbs/acre		Gain SO ₄ -S ppm lbs/acre	Rate* lbs/acre		Gain SO ₄ -S ppm lbs/acre	Rate* lbs/acre	
Flater	dry	6.6	0.85	1.4	6.2	0.81	2.1	6.3	0.82	1.1
	wet	6.9	0.89	1.5	7.1	0.89	2.13	9.7	1.2	1.6
Stewart	dry	6.6	0.85	1.4	4.9	0.63	1.5	8.4	1.1	1.5
	wet	7.5	0.97	1.6	5.3	0.68	1.8	9.6	1.2	1.7
Stewart	dry				5.4	0.70	1.9	11.3	1.3	1.8
+CaCO ₃	wet				3.0	0.39	1.1	17.8	2.0	2.8
Litter								35.6	0.46	0.64
H ₂ O		1.4	0.80	1.3	1.85	1.1	2.8	4.1	2.3	3.3

* Rate expressed as [lbs SO₄-S/acre/ppb/day] x 1000

$$\frac{\text{lbs/acre}}{\text{(soil)}} = \text{ppm} \times \text{g of soil} \times \frac{10^8}{\text{area of container}} \times 10^{-9} = \text{ppm} \times 8$$

x 0.0016

$$\frac{\text{lbs/acre}}{\text{(H}_2\text{O)}} = \text{ppm} \times 200 \times \frac{10^8}{31} \times 10^{-9} = \text{ppm} \times 200 \times 0.0029$$

TABLE 14

Sulfur uptake and pH changes under controlled atmosphere

24 ppb for 30 days

		SO ₄ - S ppm			Total S ppm			pH		
		Exposed	Control	Gain	Exposed	Control	Gain	Exposed	Control	Gain
Flater	dry	9.4	3.1	6.3	207	186	21	6.01	6.15	- 0.14
	wet	13.0	3.3	9.7	200	188	12	5.82	5.94	- 0.12
Stewart	dry	11.4	3.0	8.4	195	179	16	5.88	5.90	- 0.02
	wet	12.7	3.1	9.6	189	170	19	5.64	5.81	- 0.17
Stewart +CaCO ₃	dry	18.5	7.2	11.3	208	186	22	7.96	9.15	- 1.19
	wet	25.3	7.5	17.8	214	176	38	7.00	9.27	- 1.27
Bark (spruce)		84.2	54.2	30						
Litter (spruce)		82.3	46.7	35.6						

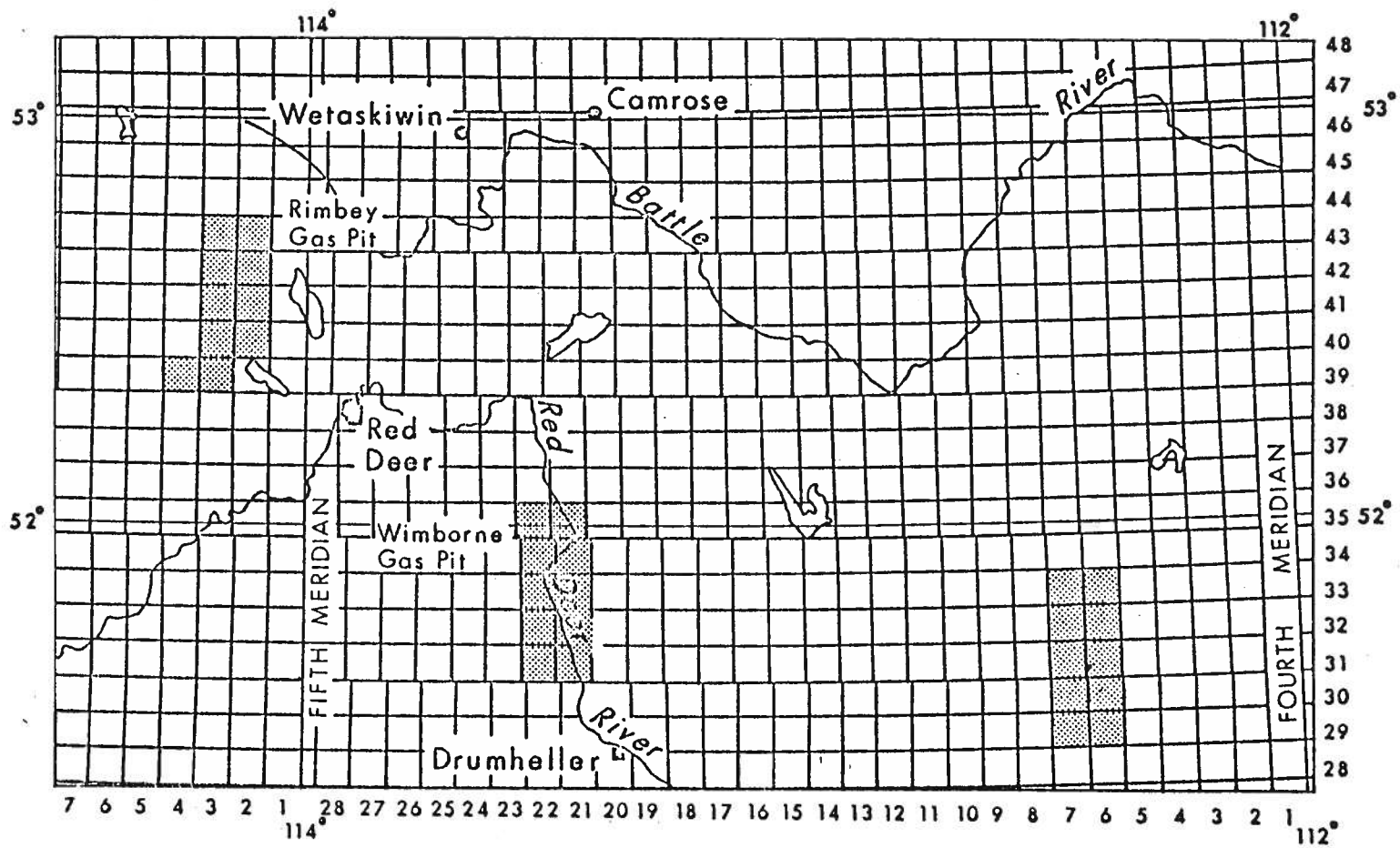


Figure 59: Situation of dustfall sampling domains in central Alberta.

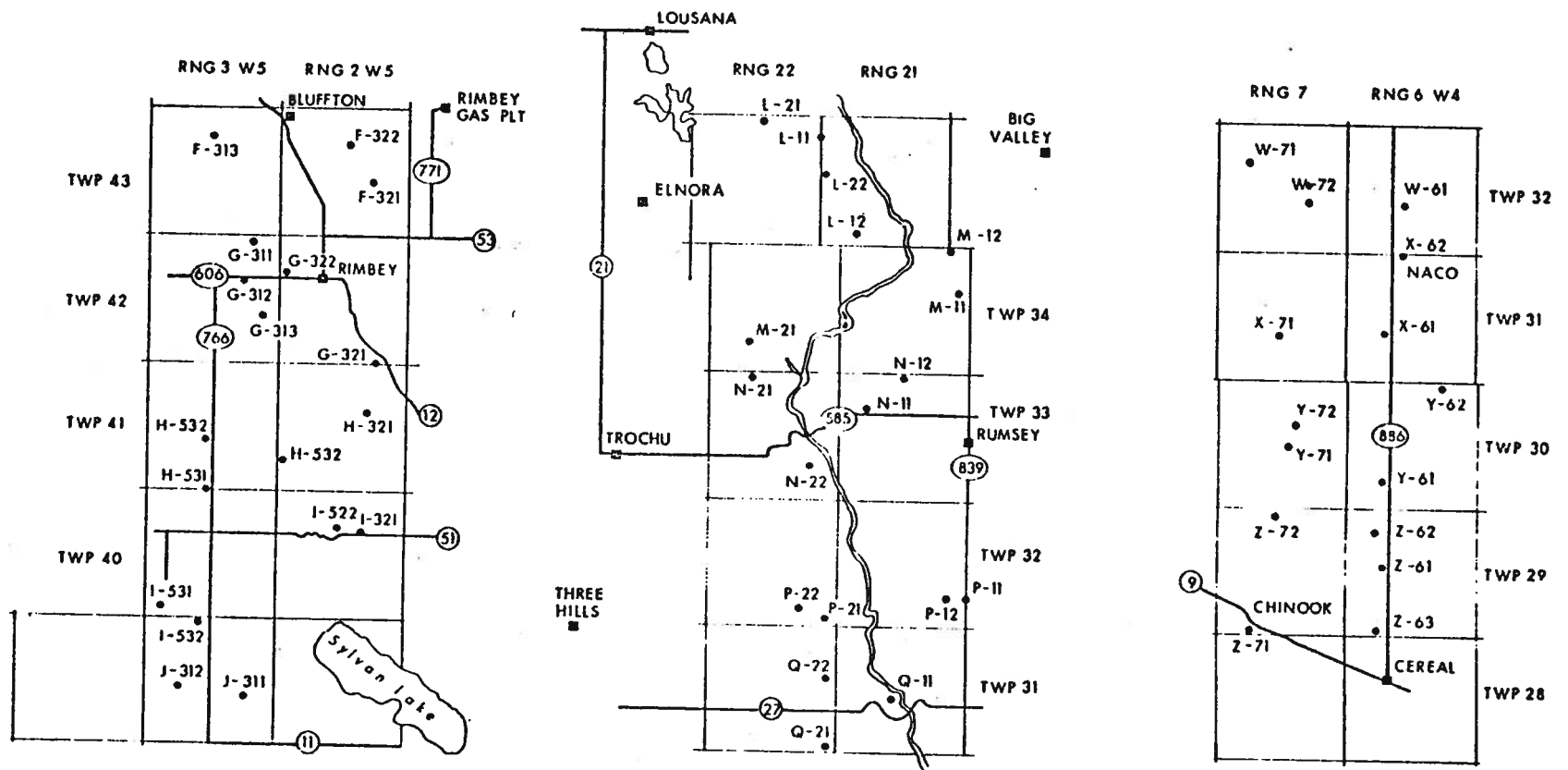


Figure 60: Location of Sampling Stations in each of the three dustfall domains.

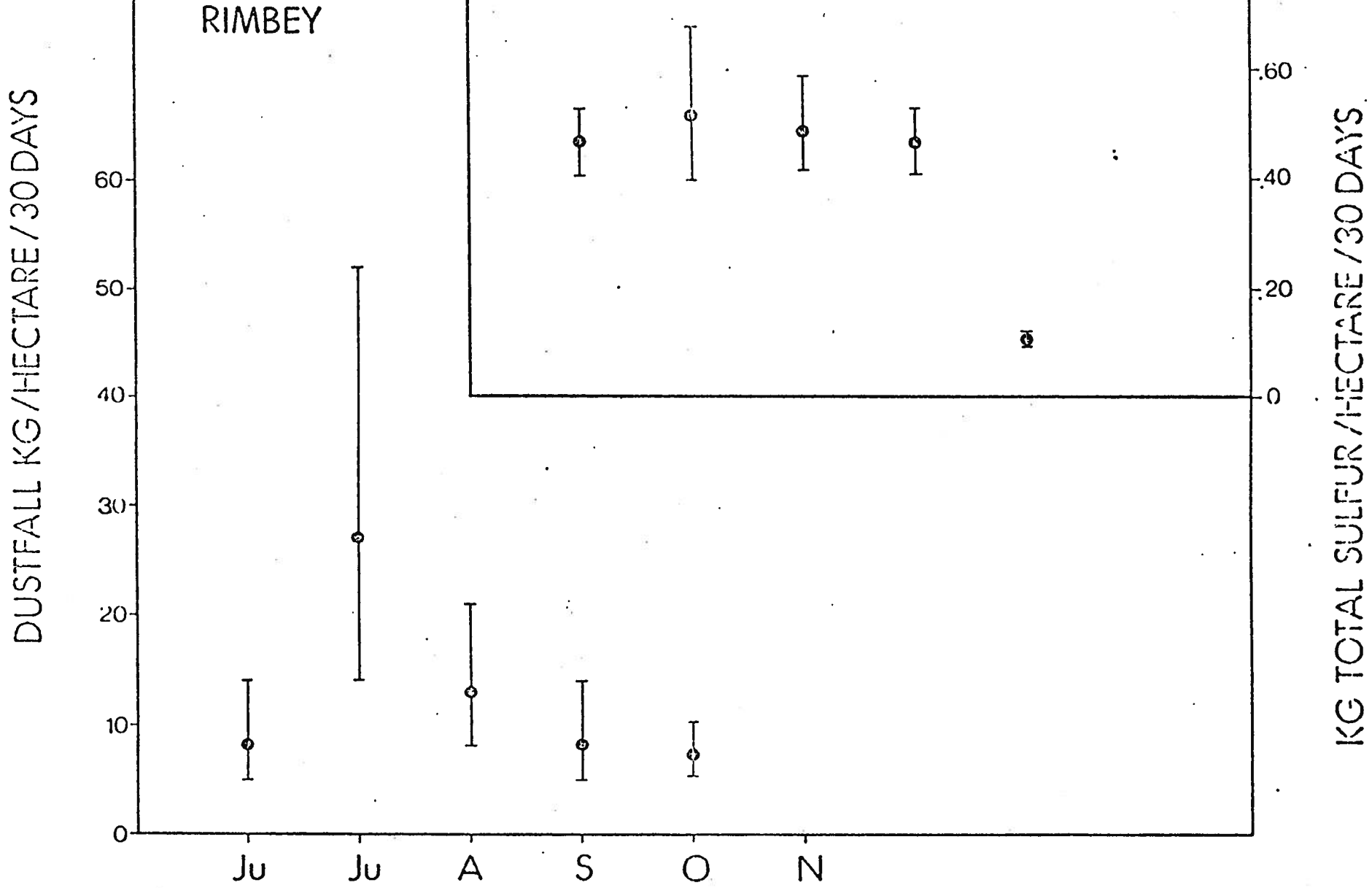
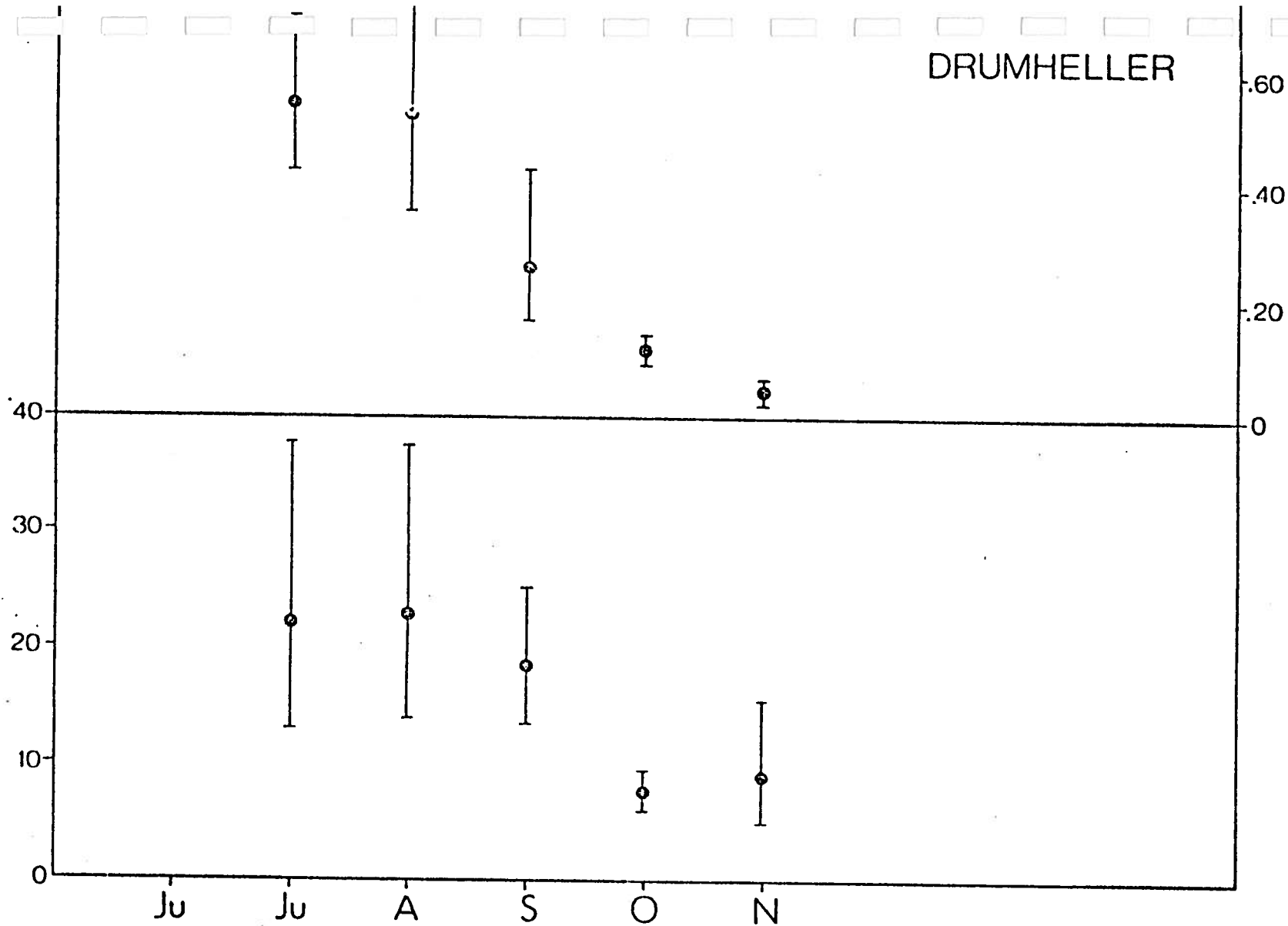


Figure 61: Rate of dustfall and sulfur deposition per hectare for the months June-November, 1975 at the indicated location.

KG DUSTFALL/HECTARE/30 DAYS

DRUMHELLER



KG TOTAL S/HECTARE/30 DAYS

Figure 62: Rate of dustfall and sulfur deposition per hectare for the months June - November, 1975 at the indicated location.

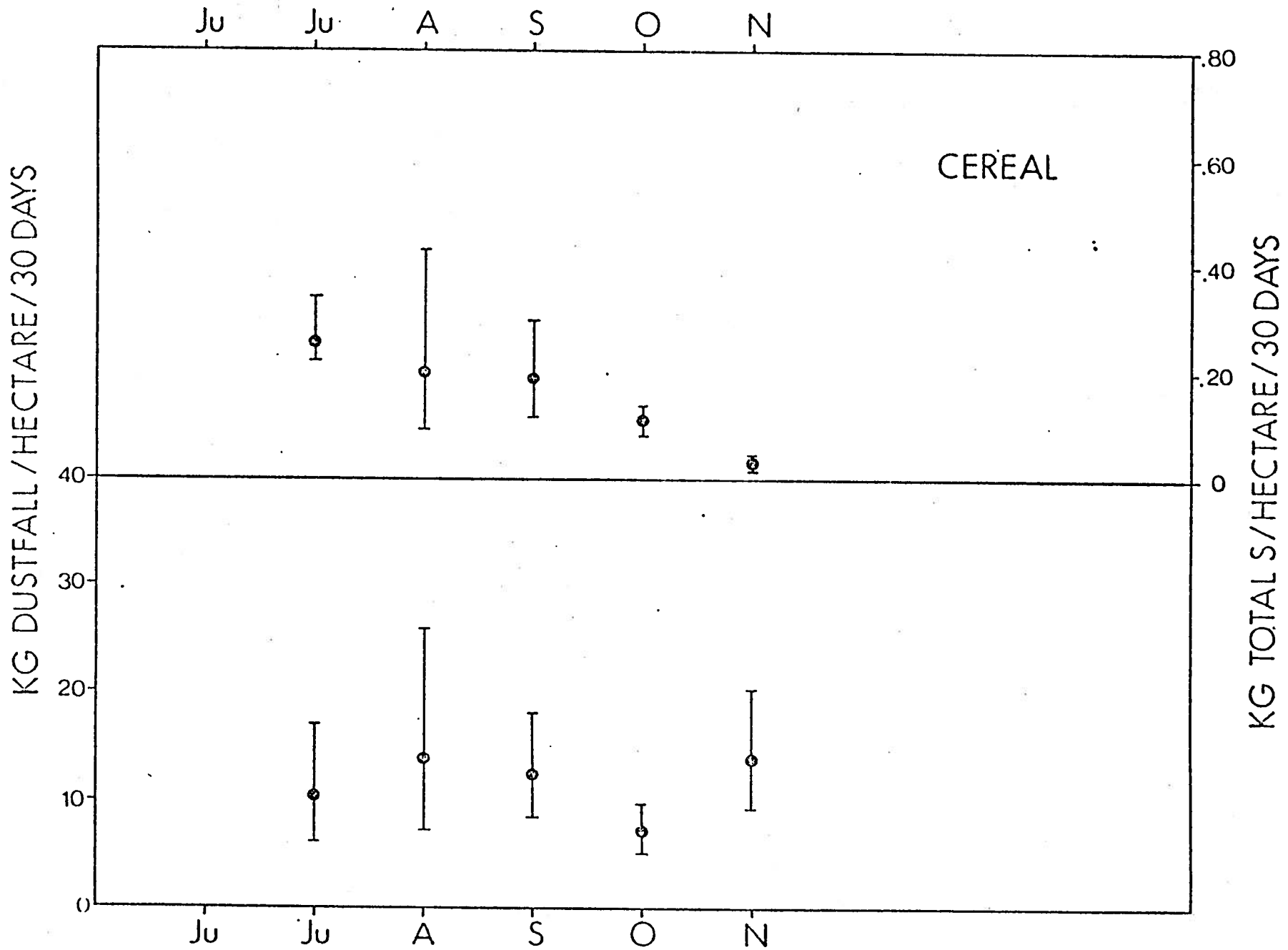


Figure 63: Rate of dustfall and sulfur deposition per hectare for the months June-November, 1975 at the indicated location.

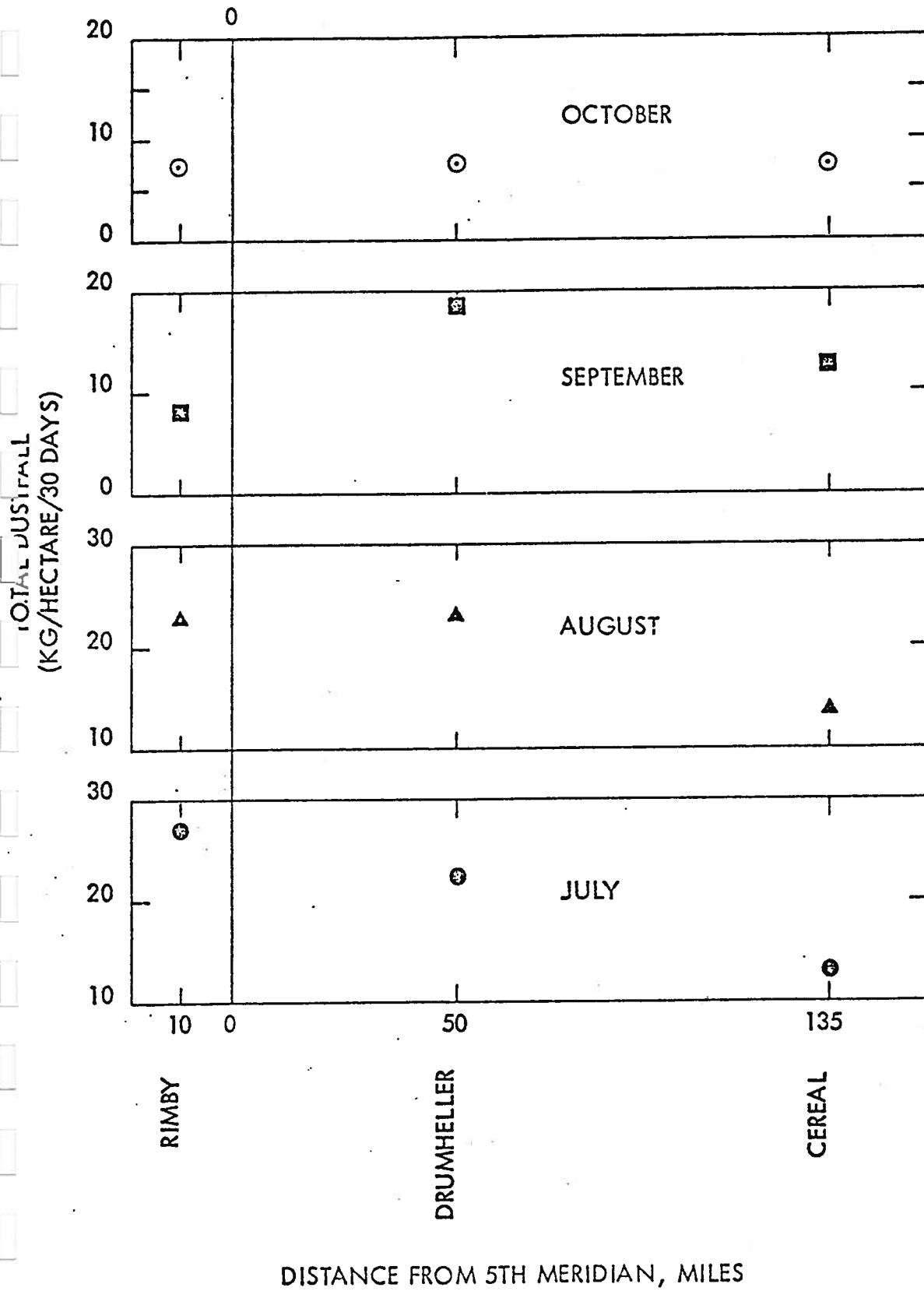


Figure 64: Total average monthly dustfall in the three sampling domains as a function of distance from the 5th meridian. July - October, 1975.

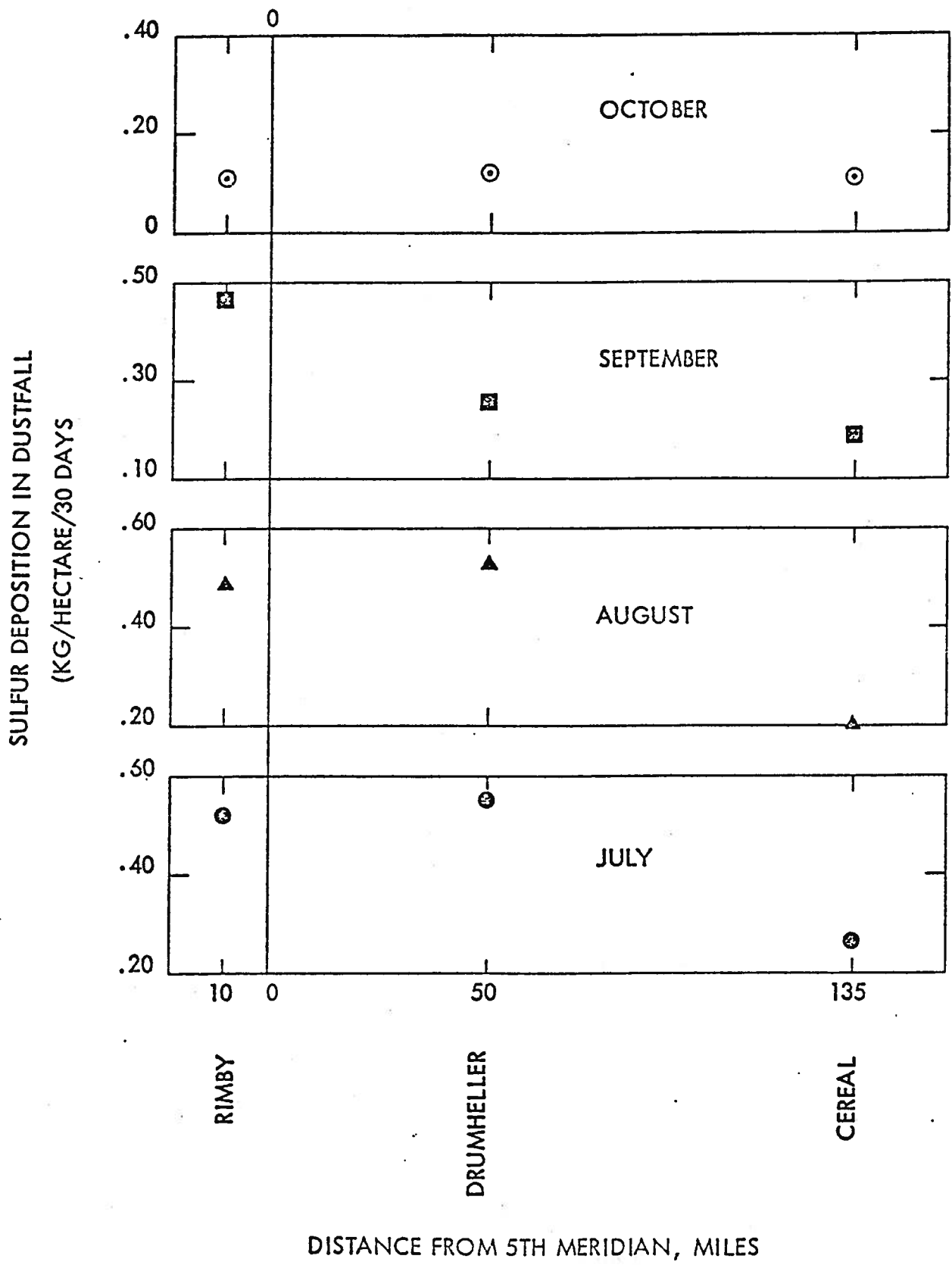


Figure 65: Average monthly amount of sulfur in dustfall in the three sampling domains as a function of distance from the 5th meridian. July - October, 1975.

KG DUSTFALL/HECTARE
JUNE - OCTOBER, 1975

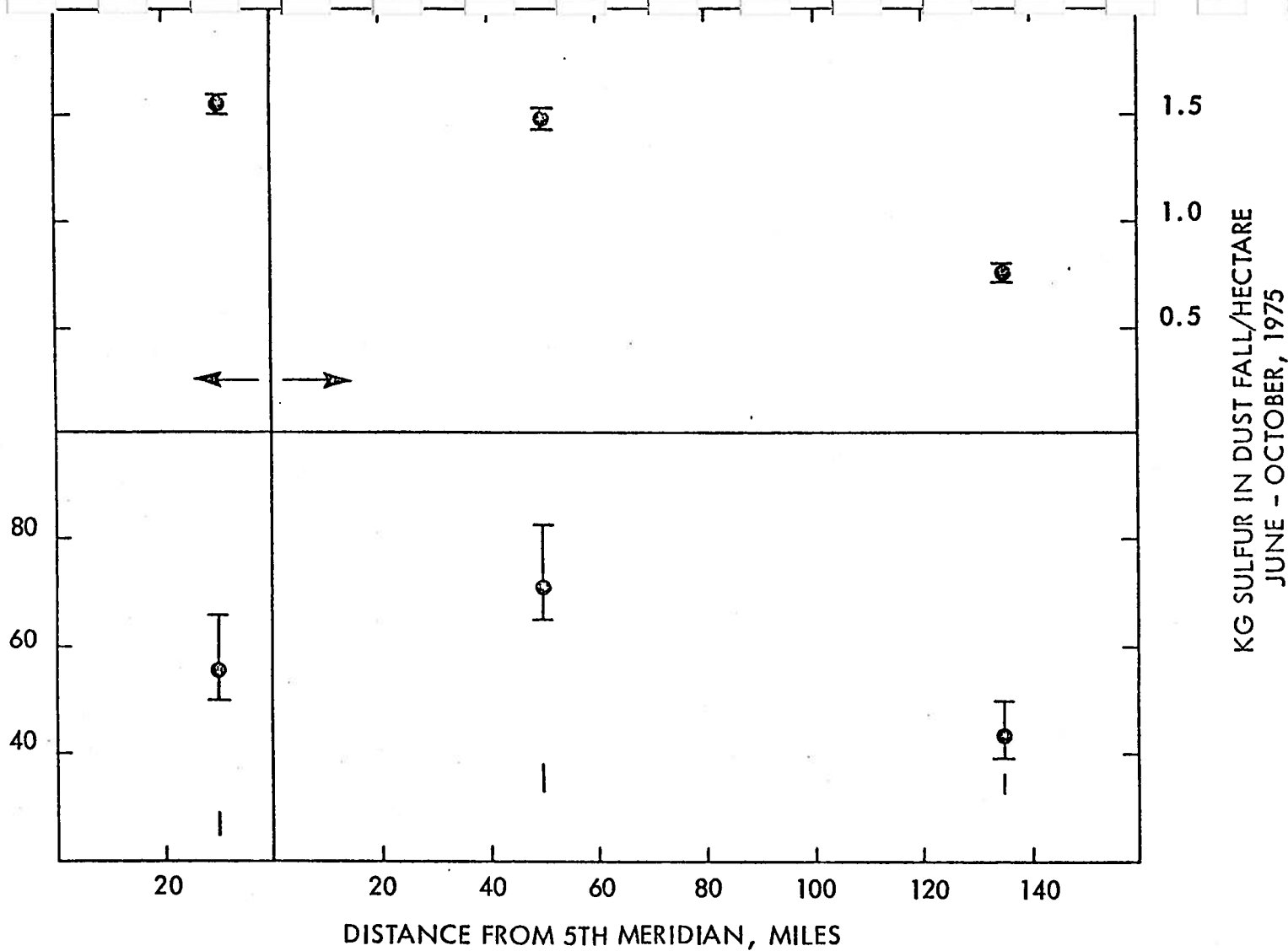


Figure 66: Total deposition of dustfall and sulfur in dustfall for the period June - November, 1975 as a function of distance from the 5th meridian.

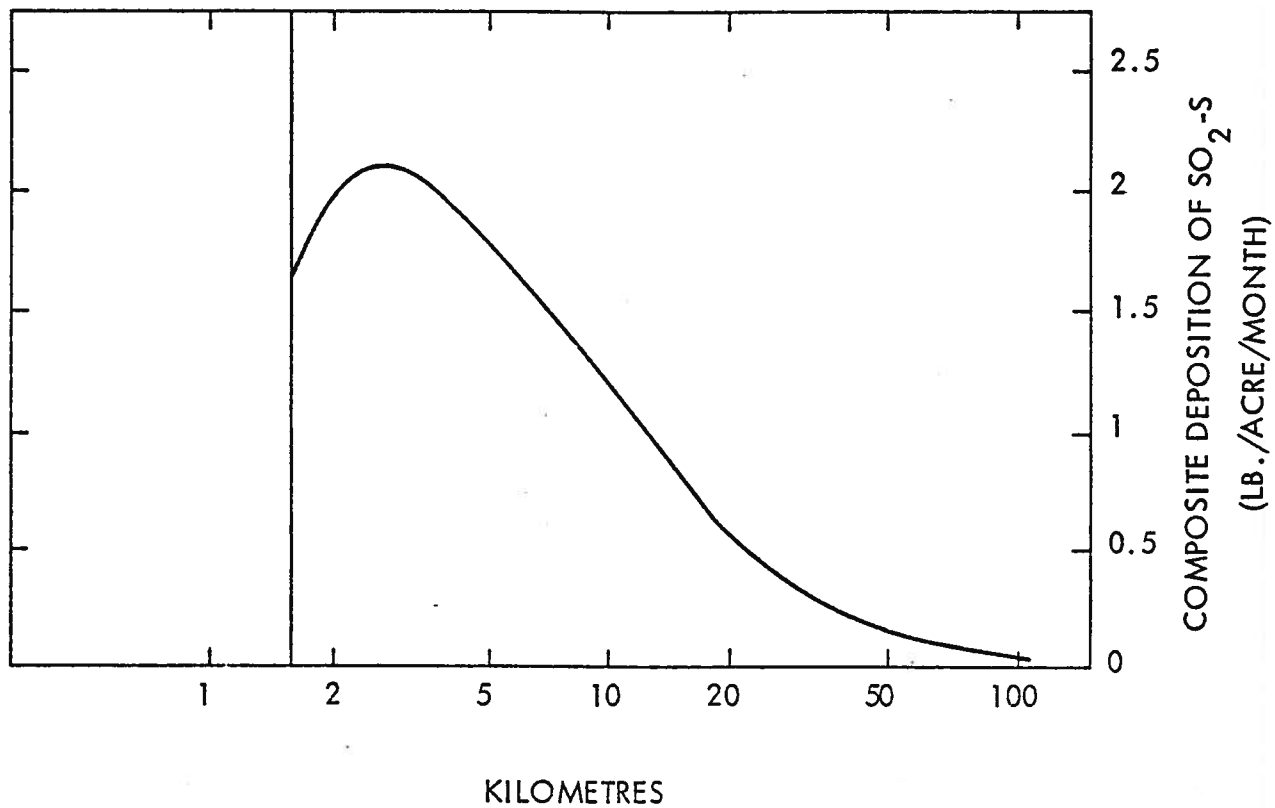


Figure 67: Composite time weighted deposition of SO₂-S as a function of distance from the east stack of the Petrogas plant for winds in the NNW sector (sector of highest wind frequency).

SO₂ settling velocity = 10^{-2} m. sec⁻¹

mixing depth = 750 meters

(Graph taken with permission from: S.F. Benjamin, "The fate of SO₂ from Sour Gas Plants," UNISUL Group 4, September 1975).

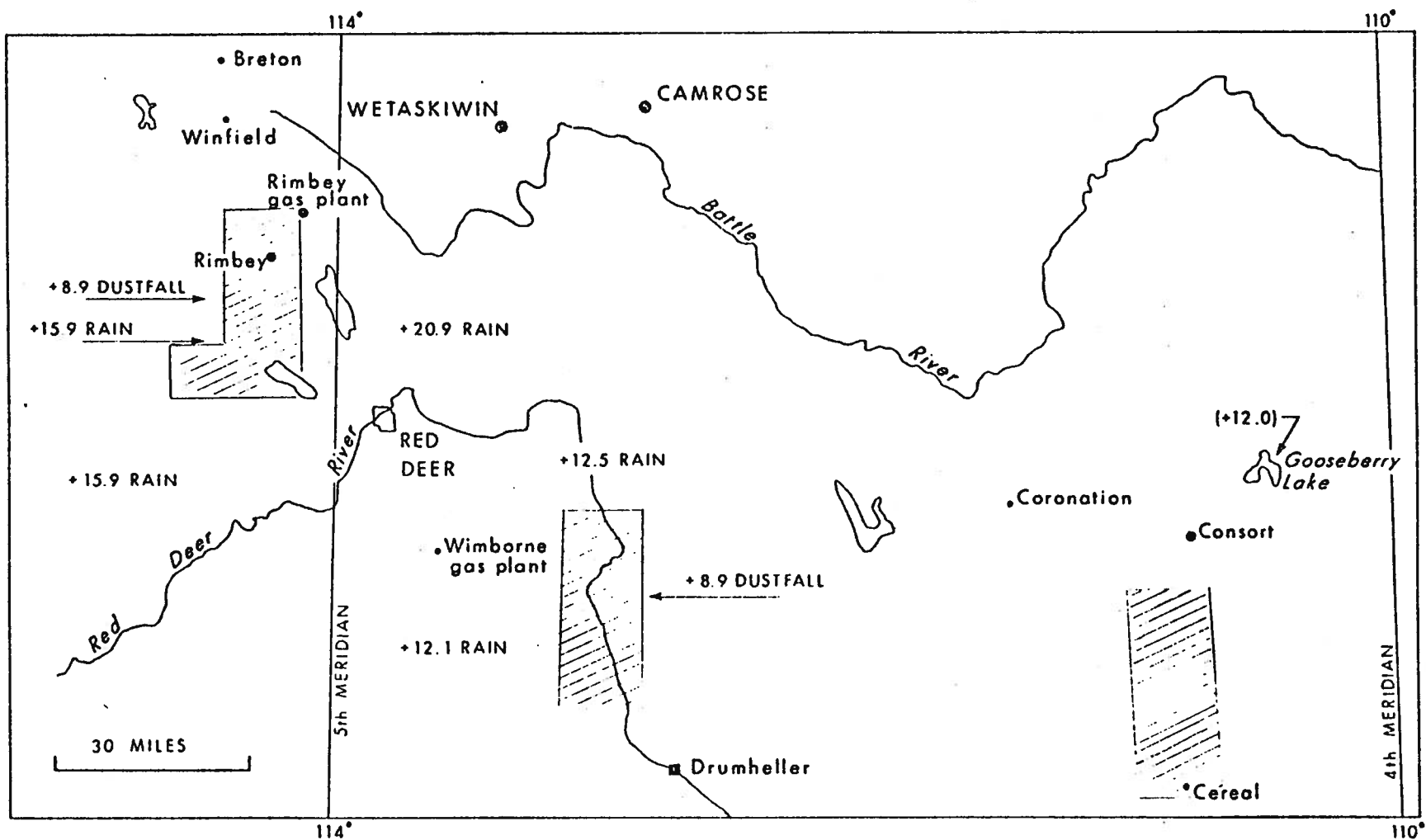


Figure 68: Geographical distribution of measured stable sulfur isotope ratios (δS^{34}).

TABLE 18

Sampling Area	Weather Station	Inches of Rainfall between Sampling Periods (from AES, Edmonton)					
		May-June	June-July	July-August	August-September	September-October	October-November
RIMBEY - ECKVILLE	Breton	1.83	4.07	2.27	2.02	0.53	0.58**
	Winfield	2.23	4.22	2.76	1.85	0.70	0.41
	Bluffton	1.87	1.70	2.17	1.39	0.30	0.39
	Rimbey	1.57	1.7(estimated)*				
	Eckville	2.78	2.36	1.06	0.79	0.45	0.64
DRUMHELLER - ELNORA	Elnora	1.56	2.29	1.89	1.34	0.45	0.62
	Wimborne	1.31	3.31	3.48	0.89		
	Huxley	1.98	1.32	1.78	0.70	0.67	0.50
	Scollard	1.46	2.48	2.00	0.44	0.37	0.55
	Drumheller	1.66	1.10	1.53	1.26	0.55	0.39
CEREAL - CONSORT	Cereal	3.57	1.42	2.06	0.79	0.27	0.46
	Wastina	---	0.34	0.54	0.40	0.28	0.29
	Sedalia	2.55	2.68	1.39	1.52	0.49	0.52
	Consort	1.94	2.73	2.82	0.51	0.57	0.41

* Not reporting after July 1, 1975

** Snowfall measured as 1 inch = 0.1 in precipitation