

## Chemical Patterns of Bulk Atmospheric Deposition in the State of Colorado

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Samples of bulk deposition from the atmosphere were taken over a 1-year interval between May 1982 and May 1983 at 42 sites distributed over the state of Colorado. Collections were complete for the entire year at 36 of these sites. The collections were made biweekly and were analyzed for major cations, major anions, total particulate material, and the hydrogen ion (*pH*). A *pH* below 5.6 was characteristic of the annual precipitation over two thirds of the state, including all of the high-elevation areas in central Colorado as well as substantial portions of the plains. The lowest *pH* values (average below 5.0) were found near the Continental Divide in the northern third and southern third of the state. Emissions of  $\text{NO}_x$  and  $\text{SO}_2$  from power plants within or near the borders of the state are of a magnitude similar to that of the total deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^- \text{N}$  within the state. Gradients of acidity within the state are to a large degree explained by three factors: (1) location of power plants and urban areas with respect to prevailing winds, (2) differential transport of strong acids and alkalis, and (3) amount of wet precipitation. At lower elevations, carbonates neutralize strong mineral acids, as shown by the distributions of strong acid anions and divalent cations. Because of their association with terrestrial particulate materials, alkalis are transported over shorter distances than the gaseous precursors of mineral acids. Thus air masses moving over the mountains, which lack large sources of either alkalis or acids, show an increasing bias toward acidifying substances at higher elevations. This causes a statewide negative relation between *pH* and elevation. Superimposed on the elevation effect is a moisture effect caused by a strong relationship between strong acid deposition and amount of wet precipitation.

### INTRODUCTION

Atmospheric deposition has been studied intensively at specific sites [e.g., *Likens et al.*, 1976] and over entire countries or regions [e.g., *Wilson et al.*, 1982]. Intensive studies at particular sites provide a degree of detail that is difficult for a large network to duplicate, but because of variation in deposition between sites, only large networks provide a satisfactory geographic overview. As an intermediate between the site-specific study and the large network, small networks giving detailed regional coverage may offer some special possibilities for the study of atmospheric deposition, but have not as yet been used very extensively (but see *Liljestrand and Morgan* [1981] and *Brezonik et al.* [1980]). This paper reports the results of a 1-year study of atmospheric deposition at 42 sites scattered over the state of Colorado. The major purpose of the study was to take advantage of the strong topographic gradients and uneven distribution of anthropogenic sources for atmospheric materials to help demonstrate some of the mechanisms of transport and effects of topographic gradients on transport.

The emphasis of this study is on transport of ecologically interesting materials rather than rain chemistry per se. Thus the data are all based on collection of total (bulk) deposition rather than the wet fraction only. While it is true that the average transport distances for particulate materials, in which dry deposition is particularly rich, are likely to be shorter on the average than those of soluble materials scrubbed out with wet precipitation, the dry fraction can account for significant amounts of transport, even over very long distances, as demonstrated by the movement of large amounts of dust from North Africa to the Caribbean [*Prospero*, 1979]. Thus for studies whose central concern is total transport, all fractions of precipitation must be included in the sampling.

Most atmospheric deposition studies have been done in or near industrialized regions. While atmospheric deposition must have been altered significantly in Colorado by human

presence, the alterations are as yet likely to be much less extensive than in most of the regions that have been studied. Thus the Colorado network study provides a view of atmospheric deposition patterns in an area still in the intermediate stages between natural background and extensively polluted. Colorado is also distinctive by comparison with most areas that have been studied in its distance from the coast. Studies at one high-elevation site in Colorado have already shown that the major ion chemistry is not appropriately viewed as a modified marine aerosol because of dominating terrestrial influence [*Grant and Lewis*, 1982]. Finally, Colorado offers an advantage for network studies in that the mountainous central portion of the state is free of significant point sources or large centers of population. This facilitates the study of transport on the basis of atmospheric deposition data.

### METHODS

Numerous kinds of collectors have been used for sampling atmospheric deposition [*Galloway and Likens*, 1976; *Galloway*, 1978]. For the network study, we needed a collector that would operate effectively at very low temperatures, would not need electrical power, and would store heavy snowfall without overflow or wind loss. Since none of the collectors in wide use met these requirements, we designed a collector that would. The collector, which is shown diagrammatically in Figure 1, consists of a piece of heavy-walled sewer pipe 25 cm in diameter. Sections of pipe 1.3 m long were used at most locations. A few collectors of 2-m length were used in areas of especially heavy snowfall. The collectors were closed at the bottom by means of a flat PVC plate that was glued to the sewer pipe cylinder. Plastic bags with the same diameter as the collector body were made to order by a bag manufacturer. These bags formed a watertight liner for the collector. The bag liner was replaced every time a collection was made.

During the summer months, when rainfall was expected to accumulate in the collector, a Plexiglas baffle was suspended about 30 cm above its bottom. The diameter of this Plexiglas plate was slightly less than the diameter of the cylinder. The bag liner of the cylinder and the Plexiglas plate were thus

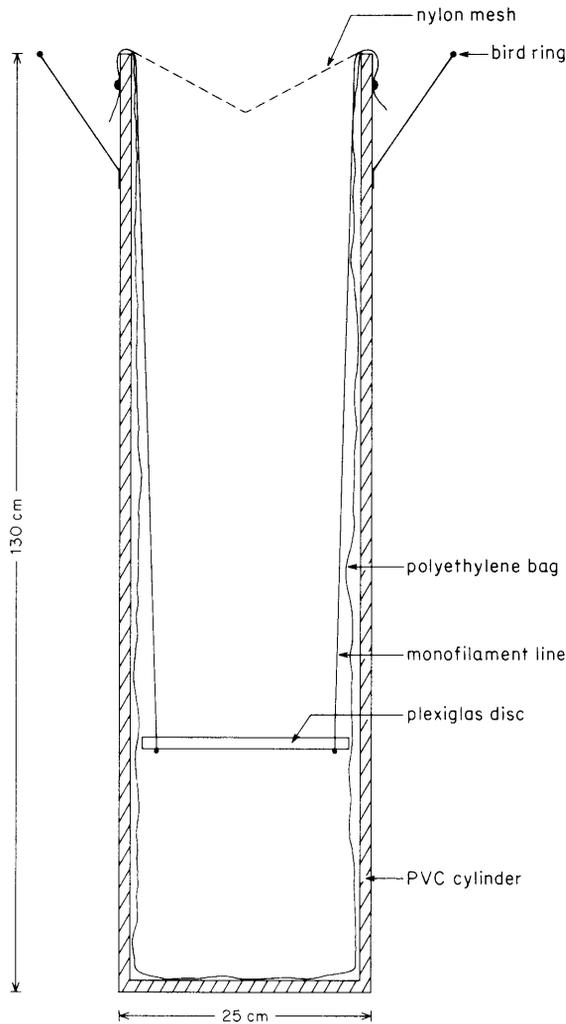


Fig. 1. Collector design.

separated by a space of a few millimeters. Wet precipitation falling on the surface of the plate ran around the side of the plate through the space between the plate and the bag wall, thus entering a chamber in the bottom part of the collector. Since this chamber had very restricted connection to the atmosphere above, evaporative loss of water was very small. It was established by a field test at high elevation that the tube collectors collect wet precipitation at rates close to those of standard weather stations [Lewis *et al.*, 1984].

During the summer, a conical piece of nylon netting was placed in the mouth of the collector (Figure 1). Insects falling into the collector could escape by walking up the screen and out of the collector rather than drowning in the water at the bottom and thus contaminating the sample. A bird ring was also placed on the top of each collector. This ring consisted of a piece of heavy-gauge insulated wire bent into a circle whose diameter was nearly double that of the collector mouth. The ring was then supported at the level of the collector mouth by stiff pieces of wire extending down to the sides of the collector. Birds inclined to perch on the collector consistently preferred to perch on the wire instead. The bird ring thus minimized the problem of fecal contamination of samples by birds. This was an especially important consideration at certain wooded plains locations but less so in more open agricultural areas or in the mountains.

Forty-two sampling stations were distributed as equally as possible over the state, as shown in Figure 2. A few of these stations proved unfeasible to operate or could only be operated for part of the year. The stations can be divided roughly into three groups on the basis of sampling duration: (1) stations where samples were taken over only a few weeks (two stations), (2) stations where samples were taken over a period of 2–6 months (four stations), and (3) stations where samples were taken over an entire year (36 stations). The locations and sampling frequencies are given in Table 1.

Collector locations were selected with considerable attention to possible local influences on atmospheric deposition. As a rule, collectors were placed more than 2 km from interstate highways and more than 0.5 km from two-lane highways. Collectors were placed upwind of roads wherever possible. Collectors were also placed a considerable distance from small dirt or gravel roads that might be an important source of dust. Most of the collectors were placed in rural areas, but a few were placed in or very near urban centers so that information on populated areas would also be available.

Collectors were held upright by means of a steel fence post. For the 1.3-m collectors, a pedestal was placed under the collector body so that the collector mouth was 2 m from the ground surface. The longer collectors (2 m) were placed directly on the ground. In areas of very heavy snow accumulation, the collectors were moved up as needed to keep ahead of snowpack.

Water that has passed through a vegetation canopy has a chemistry very different from that of free-falling precipitation [Olson *et al.*, 1981; Likens *et al.*, 1977]. For this reason, collectors were not placed beneath foliage. At the same time, it is best to situate collectors in sheltered areas because precipitation collectors of all types give the most representative samples if they are shielded from the direct influence of the wind, and the most effective shielding is natural vegetative cover. For this reason, our collectors were situated in clearings or open spaces within vegetated areas wherever possible. All precipitation collectors, including ours, are only relative indicators of actual deposition, since they fail to represent the complex sedimentation and impaction events that occur on complex vegetated surfaces.

#### Collection Schedule and Sampling Handling

Samples were collected at 2-week intervals for 1 year beginning in May 1982. At the time of sample collection, the nylon mesh and the Plexiglas plate were removed from the collector and placed on a clean surface. The waterproof bag liner was then lifted from the collector body. The sample was examined through the transparent walls of the bag and the Plexiglas plate and nylon mesh were also examined. Notes were made of the condition of the sample, with particular attention to signs of contamination. Dirt, debris, insects, or bird feces were noted if present, along with any other unusual or unexpected features of the sample.

The bag containing the sample was clamped shut at the top and inverted several times so that the water inside would rinse materials from the surface of the bag and incorporate them into the liquid component. An aliquot of the water was then removed for pH determination. A Markson 88 meter and Corning combination electrode were used for field pH determination. This meter was checked against the lab meter (see below), with which it showed excellent agreement. The temperature correction on the meter was set to the sample tem-

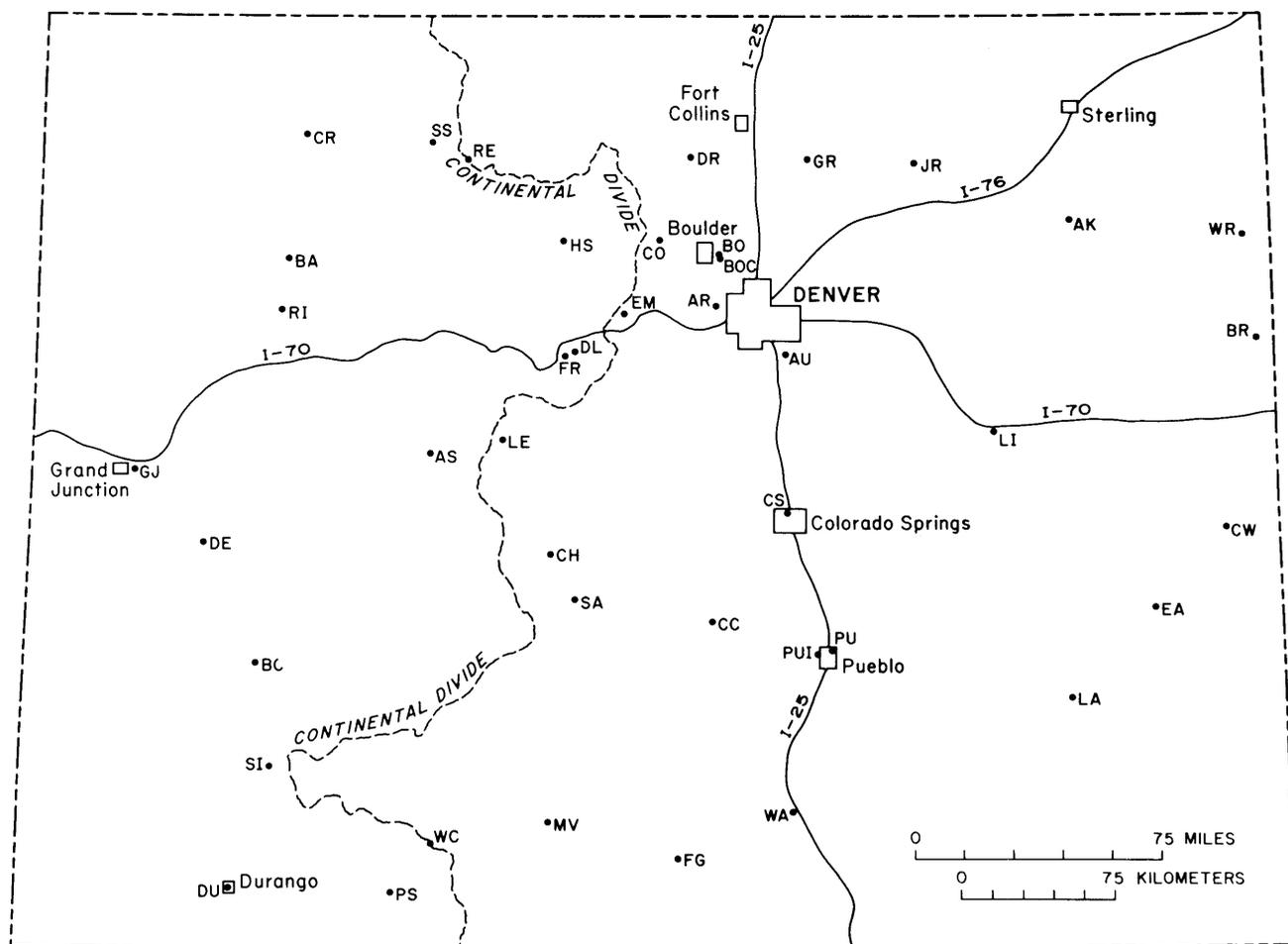


Fig. 2. Station locations.

perature, and the meter was standardized against a pair of buffers ( $pH$  4 and 7). The probes were then thoroughly rinsed to remove all traces of buffer and were allowed to sit in the precipitation sample for five minutes before the reading was taken.

After the  $pH$  was recorded, the  $pH$  subsample was returned to the bag. Although precautions were taken to prevent chemical contamination of the beaker used to hold the subsample, return of the subsample introduced a small amount of  $Cl^-$  and  $K^+$  that passed through the probe as the  $pH$  measurement was taken. A basis was developed for subtracting this contamination (see below). This very slight sample alteration was not considered important enough to warrant discard of the subsample, which would have led to other complications.

After the  $pH$  measurement had been made and the aliquot for  $pH$  had been returned to the bag, the nylon mesh and Plexiglas collector plate were rinsed with a small quantity of deionized water (100–150 mL) so that any materials that might be on these surfaces would be included in the sample. This procedure was only applicable during warm weather when the mesh and plate were in use. The rinse was done with laboratory deionized water of the same type used in laboratory chemical blank determinations. Although there might have been some argument for doing this rinsing prior to taking the  $pH$  on grounds that the material on the Plexiglas plate and on the nylon mesh might affect the  $pH$  to some extent, it was decided that any possible advantages to this

would be limited in view of the relatively small area of these surfaces and the special value of a  $pH$  measurement on a subsample that had not been diluted by rinse. If the bag contained ice or snow, it was returned to the laboratory, where it was allowed to melt completely before the mixing and  $pH$  determination were done. When there was no wet precipitation or only a trace, no undiluted  $pH$  measurement was possible. For dry samples, rinse was added (100–200 mL) and the bags were sealed and handled for subsequent analysis with the same precautions as other samples.

Samples were brought to the laboratory in Boulder from the field site. Individual samples were typically in transit for 1 to 3 days. Processing of the samples began immediately upon their arrival at the laboratory.

#### Chemical Determinations

All samples were allowed to reach room temperature before analysis began. A sample to be analyzed was thoroughly mixed inside the plastic bag and poured from the bag onto a filter tower over a dried and tared Whatman GF/C glass fiber paper (diameter 47 mm, effective pore size  $\sim 2 \mu m$ ). The entire sample was passed through the filter paper into a clean borosilicate filter flask under gentle vacuum.

After the filtration was complete, the filter was removed and placed in an oven to dry at  $60^\circ C$  to constant weight, after which it was allowed to cool in a desiccator and was reweighed on an analytical balance to the nearest 0.01 mg. This weight, after subtraction of the initial dry filter weight, yielded

TABLE 1. List of the 42 Stations and Their Elevations

Place Name	Site Code	Elevation, m
Akron	AK	1450
Arvada	AR	1790
Aspen	AS*	2430
Aurora	AU	1690
Bel Aire (near Meeker)	BA*	2160
Billy Creek (near Ouray)	BC*	2030
Boulder	BO	1570
Boulder (second collector)	BOC	1570
Bonny Reservoir	BR	1110
Canon City	CC	1630
Chalk Cliffs (near Buena Vista)	CH	2430
Como Creek	CO	2920
Craig	CR	1910
Colorado Springs	CS	1880
Cheyenne Wells	CW	1320
Delta	DE	1540
Dillon	DL	2770
Drake	DR	1910
Durango	DU	2000
Eads	EA	1290
Empire	EM	2650
Fort Garland	FG	2430
Frisco	FR	2770
Grand Junction (Clifton)	GJ	1450
Greeley	GR	1450
Hot Sulfur Springs	HS	2310
Jackson Reservoir (near Fort Morgan)	JR	1390
Las Animas	LA	1230
Leadville	LE	2920
Limon	LI	1630
Monte Vista	MV	2370
Pagosa Springs	PS	2180
Pueblo	PU	1480
Pueblo (second collector)	PU1†	1480
Rabbit Ears Pass	RE	2910
Rifle	RI	1940
Salida	SA†	2150
Silverton	SI	2830
Steamboat Springs	SS	2090
Walsenberg	WA	1910
Wolf Creek Pass	WC*	3340
Wray	WR	1110

\*4-6 months.

†1 month.

the estimate of total particulate material in the sample. The filtered water from the sample was divided into three portions: one portion for atomic absorption analysis of cations, a second for ion chromatographic analysis of anions, and a third for alkalinity and acidity determinations.

The sample portion for atomic absorption analysis (usually 50-100 mL) was treated with cesium chloride to make a concentration of 1000 ppm and with lanthanum oxide to make 10,000 ppm. The lanthanum oxide was dissolved in an HCl solution of sufficient strength to depress the subsample pH below 2.0. Atomic absorption analysis was done for the four major metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ). Blanks, standards, replicates, and spikes were run routinely to assure appropriate precision and accuracy.

The second portion of the sample, which was for anion analysis, was analyzed while still fresh with a Dionex Model 2110 ion chromatograph for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{=}$ . Duplicates, spikes, standards, and blanks were run as for the atomic absorption analysis.

The third portion of the filtered sample was analyzed for acidity, alkalinity, and pH. A Fisher Acumet Model 230 pH

meter and glass/calomel electrode pair were used for this work. The electrodes were checked against two buffer solutions (pH 4, 7) prior to use. The electrodes were then rinsed copiously with distilled water to assure complete removal of the buffer solutions. A 25-mL subsample of the filtered water was withdrawn with a volumetric pipet and placed into a beaker. The rinsed electrodes were lowered into the beaker over a stir plate and a small, clean stirring bar was added and allowed to run at low speed. The electrodes were then allowed to equilibrate. It was determined empirically that complete equilibration occurred within 5 minutes, so the equilibration time was standardized at 5 minutes. In some rare instances where the pH was not stable after 5 minutes, a longer equilibration time was allowed. After equilibration, the initial pH was recorded. The tip of a microburet was then lowered into the subsample. The microburet contained  $\text{H}_2\text{SO}_4$  of known molarity in the vicinity of 0.02 M. A small increment of acid (usually 0.01 mL) was dispensed into the beaker from the microburet, and the new pH was read after a stable reading could be obtained. This was repeated until the pH of the sample reached 4.0. After this titration was complete, a second titration was done on another 25-mL subsample using 0.02 M NaOH and titrating in the upward direction. The pH response curve to the addition of strong acids and strong bases was thus established.

#### Computations

The acid-base titrations were analyzed by the method of Gran [1952] as illustrated by Stumm and Morgan [1982] for the carbonate-bicarbonate-carbon dioxide system. The purpose of this procedure was to provide estimates of the volumes of titrant required to reach the bicarbonate- $\text{CO}_2$  equivalence point (pH ~ 5) and the bicarbonate-carbonate equivalence point (pH ~ 8). The method is based on the principle that the hydrogen ion concentration in the solution changes linearly in approaching either of the two equivalence points from either direction. Thus linear regression can be used to extrapolate a line whose intersection with the axis representing the volume of titrant is the amount of titrant required to reach the equivalence point. Regressions of this type were done for each of the two equivalence points on all of the samples. The advantage of the Gran procedure is that it produces a much better estimate of the endpoints of the titration than could simple examination of the titration curve. Furthermore, this method does not rely on absolute correspondence between pH measurements and hydrogen ion activities [Stumm and Morgan, 1982].

Because precipitation is a mixture of substances rather than simple combination of pure water and inorganic carbon species, some assumptions of the Gran procedure do not apply in the strictest sense. However, nonlinearities resulting from the presence of other materials are typically so insignificant as to have a minor influence on the results, as shown by theoretical considerations [Stumm and Morgan, 1982] and by the plots for individual samples. In instances where there appeared to be nonlinearity or where the titration was improperly done, as indicated by regression  $r^2 < 0.90$ , the endpoints were set equal to the average for the series.

In many of the precipitation samples the initial pH was below the bicarbonate- $\text{CO}_2$  equivalence point and in almost all the rest of the samples it was between the two equivalence points. In samples of either category the total amount of base required to titrate to the upper equivalence point (carbonate-bicarbonate) is the total acidity of the sample. If the initial pH is between the two points, then the total acidity is entirely

accounted for by weak acids. If the initial pH is below the bicarbonate-CO<sub>2</sub> equivalence point, then the amount of base required to move up to the first equivalence point is a measure of the concentration of strong acids in solution and the residual amount required to reach the second point is a measure of the weak acids in solution. In such a case the sum of strong acid acidity and weak acid acidity is the total acidity of the sample.

For convenience we equate the weak acids with bicarbonate. In actuality, some of the weak acid acidity may be accounted for by certain organic acids or other proton donors known or suspected to contribute to the acidity of precipitation [Galloway *et al.*, 1976a, b]. Bicarbonate is the principal contributor to weak acid acidity, but to assume that 100% of the weak acid acidity is due to bicarbonate is a simplification.

As mentioned in connection with the discussion of field pH measurements, a correction was necessary for the contamination of the field pH aliquot with potassium and chloride coming from the ceramic pin of the pH probe used to take the field pH measurements. Probes were allowed to stand in rainwater of known chloride concentration for 5 minutes in several trials and the amount of chloride leaking from the probe over this time interval was determined by reanalysis of chloride using the ion chromatograph. The mean chloride leakage amounted to 3.25  $\mu\text{g}$  in 5 minutes. Since this amount of chloride is extremely small in relation even to the lower amounts of chloride found in the sample series, the contamination is of negligible consequence and was therefore disregarded.

Since the analyses were done on samples that sometimes incorporated a small amount of deionized water used for rinsing purposes, all of the measured concentrations were corrected for dilution prior to further data processing. Concentrations were then converted to deposition rates expressed as milligrams per square meter per week. This was accomplished by multiplying the concentration of the sample times the sample volume to obtain the weight and dividing the weight by the area of the opening at the top of the collection cylinder and then by the amount of time over which the collection extended (almost always 2 weeks). Although the concentration data will be given some attention, the key data here are the deposition rates.

## RESULTS AND DISCUSSION

### *Some General Properties of the Sample Series*

The total number of samples was 943. All data for samples that showed some sign of contamination were discarded, and this reduced the number of valid samples to 820. Typically the number of analyses for a given variable was slightly less than this, due to occasional loss of sample splits or other problems with individual analyses. The number of valid analyses for a particular variable is thus usually between 750 and 800.

The mean volume of water in the collectors for the entire sample series was 760 mL. Since the collecting area was 506 cm<sup>2</sup>, this corresponds to an average of 15 mm per collector per two-week period. Nine percent of the collections contained either no moisture or only a trace of moisture (less than 10 mL). Rinse was added to 64% of the samples. The average amount of rinse added was 72 mL, or somewhat less than 10% of the average sample volume.

Since the pH of samples was taken once in the field and a second time in the lab as part of the alkalinity titration, a comparison of the stability of pH under various conditions is

TABLE 2. Means for the Entire Data Set (All Stations)

Variable	Deposition			Composite Concentration*	
	mg/m <sup>2</sup> /week		meq/m <sup>2</sup> /week	mg/L	meq/L
	Mean	Standard Error			
<i>Cations</i>					
Ca <sup>++</sup>	5.83	0.20	0.292	0.77	0.0385
Mg <sup>++</sup>	0.66	0.03	0.054	0.087	0.0071
Na <sup>+</sup>	1.89	0.12	0.082	0.25	0.0109
K <sup>+</sup>	2.47	0.13	0.063	0.33	0.0084
H <sup>+</sup>	0.050	0.0039	0.050	0.0063	0.0063
<i>Anions</i>					
HCO <sub>3</sub> <sup>-</sup>	10.6	0.97	0.174	1.40	0.0230
Cl <sup>-</sup>	4.43	0.29	0.125	0.58	0.0163
SO <sub>4</sub> <sup>=</sup>	14.1	0.62	0.294	1.86	0.0387
NO <sub>3</sub> <sup>-</sup> N	2.70	0.12	0.193	0.36	0.0257
<i>Total Particulates</i>					
	167.	6.7	...	22.0	...

\* $\Sigma$  deposition/ $\Sigma$  water.

possible. The difference between average field pH and average lab pH was 0.08 (the average lab pH was slightly higher than the average field pH). This difference is not very great in view of the transport interval that separates the two measurements as well as the differing measurement conditions, different pH meters used to make the measurements, and the need for samples to approach complete chemical equilibrium after mixing the wet precipitation with the dry portions of the sample on the walls of the bag. Furthermore, elevation change in some cases would be responsible for some small changes in pH.

Complete ion balances cannot be done on the data because ammonium, which makes a significant contribution to cations, was not analyzed. However, since all other major constituents were analyzed, a comparison of cation and anion equivalents is informative. The anion mean was 0.77 meq/m<sup>2</sup>/week and the cation mean was 0.54 meq/m<sup>2</sup>/week. The means thus show the expected cation deficiency caused by exclusion of ammonium from the cation total. These averages imply a deposition of ammonium equal to 0.23 meq/m<sup>2</sup>/week, which is reasonable [cf. Grant and Lewis, 1982; Lewis, 1981], especially in view of the inclusion of agricultural areas in the sample series.

### *Chemical Characteristics of the Pooled Data Set*

It is useful to consider the entire data set as a frame of reference for the individual stations. Table 2 summarizes the mean characteristics of bulk deposition at the 42 stations. Columns two through four in Table 2 show deposition expressed both as milligrams and as milliequivalents. The last two columns of the table express precipitation chemistry in terms of concentrations. The concentrations are composite averages, which are obtained by dividing the total annual deposition by the total amount of water. Another method of obtaining concentrations is by volume weighting. Volume-weighted concentrations are the summed products of the concentration and the liquid volume of the sample on each date divided by total annual volume. The difference between a composite average and a volume-weighted average can be clarified by an example: a collection interval during which there was no wet precipitation will contribute to the deposition sum used in the composite average but will get a zero weighting in the volume-weighted averaging. Composite averages are more correct for

TABLE 3. Means for the Entire Data Set for Variables of Special Relevance to Acidity

	Mean	Standard Error
<i>Concentration</i>		
pH	5.72	0.02
H <sup>+</sup> , $\mu\text{eq/L}$ (composite average)	6.30	...
H <sup>+</sup> , as pH*	5.20	...
<i>Deposition</i>		
H <sup>+</sup> , $\mu\text{eq/m}^2/\text{week}$	50.	3.9
Total acidity, $\mu\text{eq/m}^2/\text{week}$	224.	16.1
Strong acidity, $\mu\text{eq/m}^2/\text{week}$	49.	5.1
Strong acid anions, $\mu\text{eq/m}^2/\text{week}$	488.	20.

\*Average H<sup>+</sup> converted to pH.

present purposes, but the volume-weighted averages differ from the composite averages by at most 5%.

Calcium is the dominant cation in precipitation but is closely followed by sodium and potassium. Given the amounts of ammonium implied by subtraction of measured anions and measured cations, it appears that ammonium would rank close to calcium in its contribution to total cations (0.23 meq/m<sup>2</sup>/week). Next in the sequence would be sodium, then potassium, magnesium, and the hydrogen ion. These relative contributions to cation totals contrast with data from coastal areas, where sodium is likely to be the dominant cation on a milliequivalent basis [Gorham, 1976]. In fact, the dominance of sodium is so widespread for precipitation that one of the models used for precipitation chemistry assumes a marine source for the aerosol cations [Granat, 1972], but such an assumption would clearly not apply to Colorado.

Among the anions, sulfate is dominant, and is followed by bicarbonate, nitrate, and chloride. Nitrate is surprisingly high in relation to sulfate, and both sulfate and nitrate are very high with respect to chloride, indicating significant alteration of precipitation either by gaseous sulfur and nitrogen oxides or some combination of these plus sulfate derived from mineral sources. Total particulate material is in the range expected from other studies [cf. Lewis, 1981; Grant and Lewis, 1982].

Table 3 summarizes information for variables of special relevance to acidity of precipitation. The mean pH of the samples that were not entirely dry was 5.72. Another approach that is really more valid for obtaining the representative acidity of precipitation is to obtain the composite average for the H<sup>+</sup> ion and then convert the average to pH. This avoids averaging the logarithms. When this is done for the network sample set, the average pH is 5.20. The pH is lower when the concentrations instead of the logarithms are averaged because the average concentration is greatly affected by the highest 10% of observed hydrogen ion concentrations.

Table 3 also shows acidity in terms of deposition rates. The average total acidity is 224  $\mu\text{eq/m}^2/\text{week}$ , which is 4 to 5 times as high as the free hydrogen ion deposition. Strong acidity is virtually identical to the average observed H<sup>+</sup> ion deposition because the average H<sup>+</sup> ion deposition is determined principally by the strongly acidic samples. Strong acid anions total over twice the total acidity. This suggests that sulfuric and nitric acids are partly neutralized by bicarbonate.

Figure 3 shows histograms of the frequency of four of the variables of special interest with respect to acidification. The frequency distribution of pH is shown in the upper left-hand panel. The frequency distribution is slightly bimodal, with one

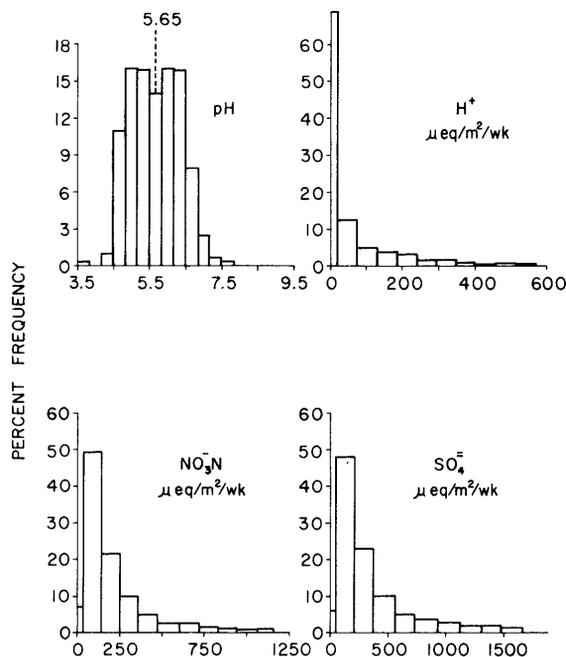


Fig. 3. Frequency distributions of selected variables.

peak in the vicinity of 5.0 and a second in the vicinity of 6.0. Geographic and other explanations for this will be evident below. Frequency distributions of deposition rates for the hydrogen ion and for the two major strong acid anions show a great deal of skew. In each case, because of the skew, the average will be influenced to an exceptional degree by samples on the tail of the distribution.

#### Moisture, Elevation, Point Sources, and Wind

The amounts of wet precipitation collected over the year of study are summarized in Figure 4. The patterns shown in Figure 4 compare very favorably with the wet precipitation patterns expected from long-term averages in Colorado (e.g., the U.S. Geological Survey Normal Annual Precipitation Map for 1931–1960). Variations associated with steep changes in terrain and complex topographic features are, of course, not resolved by Figure 4.

Figure 4 shows that the stations can be divided into groups according to amount of wet precipitation over the period of study. Very dry stations include four in the south-central por-

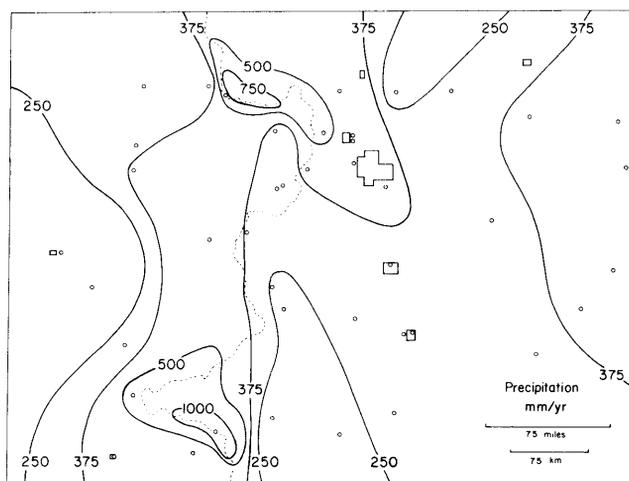


Fig. 4. Wet precipitation at the 42 stations.

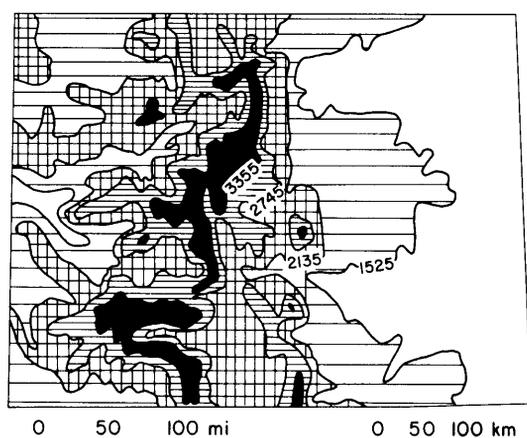


Fig. 5. Elevation map [after Hammerson, 1981].

tion of the state, one at Greeley, and two in the Grand Junction area. In the next highest category are some stations in the western portion of the state and stations over a large portion of the central and east-central portion of the state. Still higher wet precipitation was characteristic of a block of stations in the extreme eastern part of the state and in a corridor extending from north to south near the Continental Divide. This corridor lies toward the west of the divide in the southern half of the state and toward the east of the divide in the northern half of the state. Finally, there is a group of very wet stations, all of which are at high elevation (Figure 5). It is also clear from comparison of Figures 4 and 5, however, that not all sites at high elevation received large amounts of wet precipitation.

Concentrated sources of substances likely to alter precipitation chemistry include urban areas and power plants. Urban areas are mainly concentrated in the Front Range (Figure 2). Table 4 lists the major power plants in Colorado and their approximate emission rates for  $\text{SO}_2$  and  $\text{NO}_x$  (Environmental Protection Agency (EPA) Denver Office, personal communication). The total emissions estimates are based on the hourly  $\text{SO}_2$  and  $\text{NO}_x$  emissions for times of normal plant operation.

These hourly figures have been multiplied by 0.8 (a conversion factor supplied by the EPA) to correct for periods of reduced output. In addition,  $\text{SO}_2$  and  $\text{NO}_x$  have been converted to  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  for direct comparison with the atmospheric deposition study. Numerous small power plants are omitted from the list. The table includes the Four Corners power production facilities because they are close to and upwind of Colorado. There is a copper-smelting operation in Utah directly to the west of Colorado, but it is not included in Table 4 because of its distance from the state border. There are several power plants in Wyoming just north of the Colorado state line, but prevailing winds are not likely to carry most of the atmospheric materials from these plants into Colorado.

Since the absolute release rates of  $\text{NO}_x$  and  $\text{SO}_2$  for the power plants are very difficult to put into perspective with atmospheric deposition data, we have expressed the release rates in relative terms in the last column of Table 4 and in Figure 6. The basis for these relative figures is the annual average weekly release from each plant divided by the area of the state. This converts the release rates to the same dimensional basis as the atmospheric deposition rates (milligrams per square meter per week). Such a calculation should not be taken to imply that all the emissions of the power plants are deposited as  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  within Colorado. Emissions expressed in this form do, however, provide a basis for judging whether the releases of power plants are of sufficient magnitude to be a major consideration in accounting for deposition of strong acid anions and strong acidity.

Air movement is also relevant to the interpretation of atmospheric deposition data. Air movement in Colorado is especially complex, and synoptic data are surprisingly scarce. Figure 7 shows an overview (N. Doesken, Colorado State Climatologist's Office, personal communication, 1983). In the upper atmosphere (mountaintop level and above), prevailing winds are from the west over the entire state. This pattern is characteristic of all seasons, although it is less pronounced in summer than winter. There is some irregular shifting between northwesterly and southwesterly, giving an average direction of movement that is very nearly due west to due east. At ground level, air movement is very complex and can be

TABLE 4. Emissions Expressed on an Absolute Basis and Relative to Land Area of Colorado

Location	Plant Name	Emissions During Operation, lbs/hr*		Emissions, mg/m <sup>2</sup> /week†	
		SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup> N
<i>Colorado Sites</i>					
Craig	Craig	3200	1800	0.97	0.17
Hayden	Hayden	6900	4000	2.09	0.38
Brush	Pawnee	6000	3500	1.82	0.33
Boulder	Valmont	1800	1000	0.55	0.09
Denver	Cherokee	8400	4900	2.54	0.47
Denver	Arapahoe	2800	1600	0.85	0.15
Colorado Springs	Drake	3240	1900	0.98	0.18
Colorado Springs	Nixon	2400	1400	0.73	0.13
Pueblo	Commanche	8400	4800	2.54	0.46
Subtotal		43140	24900	13.1	2.36
<i>Other Sites</i>					
Four Corners (approximation)	...	24000	13900	7.27	1.32
<i>Grand Totals</i>					
		67140	38800	20.4	3.68

\*Source: EPA, Denver

†Annual average milligrams of emission per square meter of state (see text).

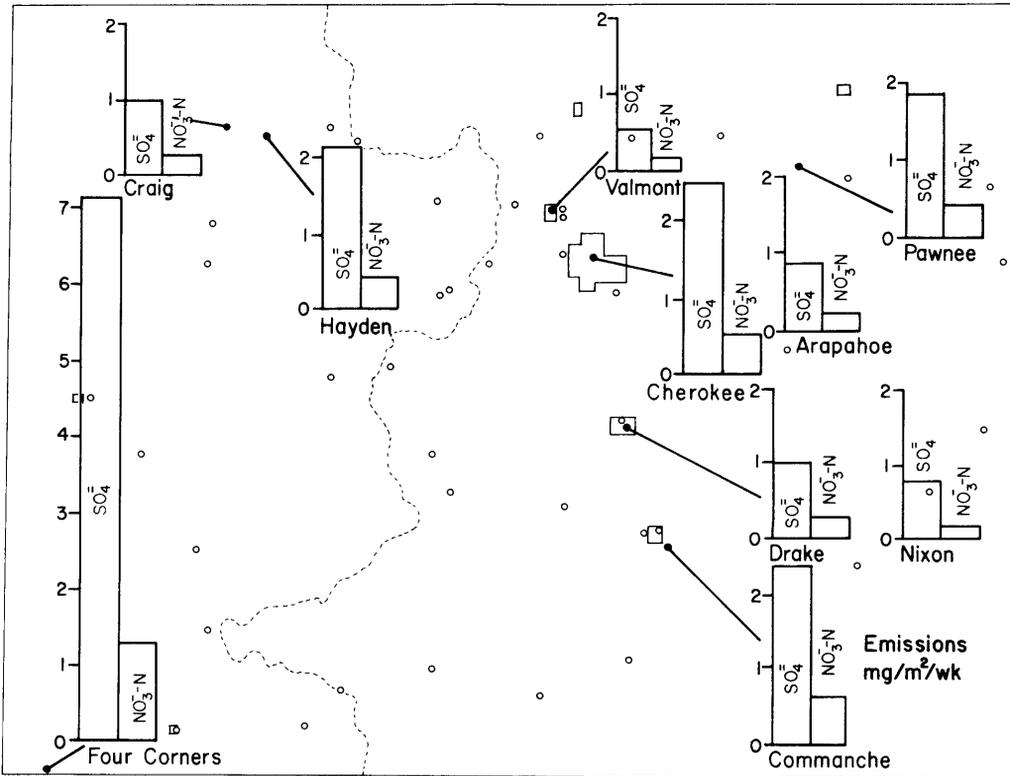


Fig. 6. Major power plants and their emissions expressed as  $SO_4^-$  and  $NO_3^-N$  per unit area of the state.

strongly influenced by local topography. Some general patterns can be identified, however. On the West Slope beyond the steepest terrain, and in large relatively flat areas at high elevation, the prevailing movement is from the southwest all

year. East of the Continental Divide, warm season winds blow from the southeast, while in cold weather the prevailing winds tend to be from the northwest. In and near the mountains, valley circulation patterns often dominate local airflows

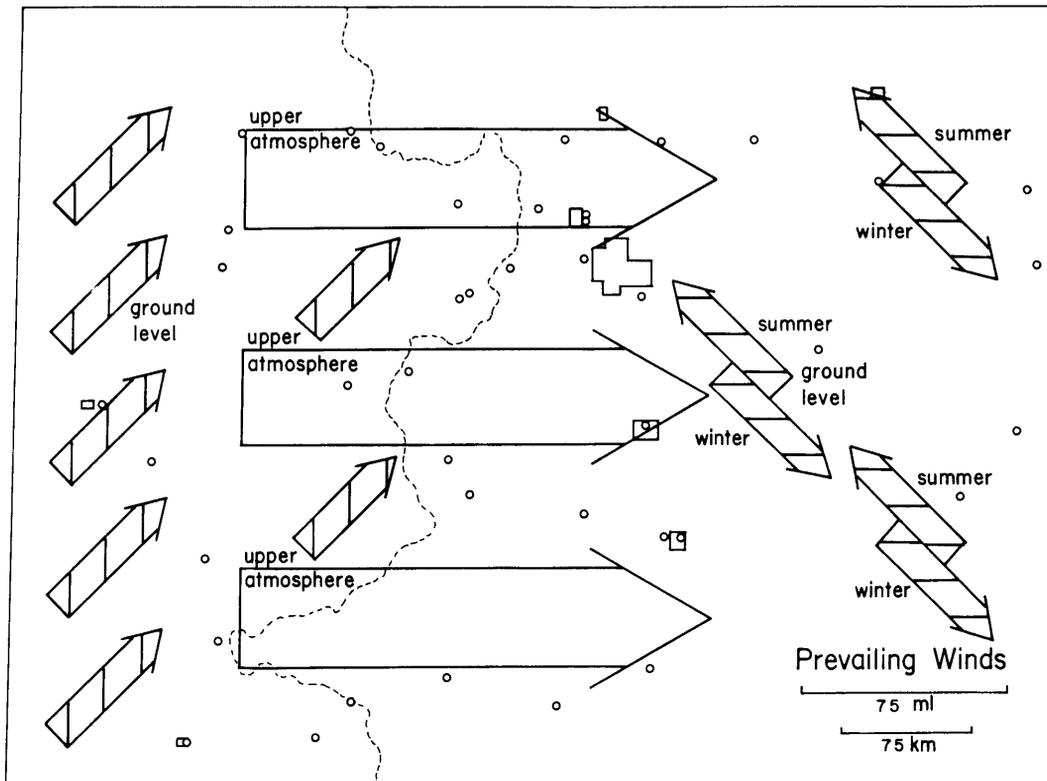


Fig. 7. Prevailing winds.

TABLE 5. Results of Multiple Regression Analysis for Log of Deposition Rate (Dependent Variable) Versus Elevation and Wet Precipitation (Independent Variables)

	Multiple R		Significant Relationships ( $p < 0.05^*$ )
	For Elevation	For Elevation and Wet Precipitation	
Ca <sup>++</sup>	0.59	0.72	elevation (-), wet precipitation (+)
Mg <sup>++</sup>	0.37	0.56	elevation (-), wet precipitation (+)
Na <sup>+</sup>	0.09	0.35	neither
K <sup>+</sup>	0.39	0.41	elevation (-)
SO <sub>4</sub> <sup>=</sup>	0.02	0.75	wet precipitation (+)
Cl <sup>-</sup>	0.19	0.21	neither
NO <sub>3</sub> <sup>-</sup>	0.31	0.87	wet precipitation (+)
HCO <sub>3</sub> <sup>-</sup>	0.77	0.78	elevation (-)
H <sup>+</sup>	0.74	0.79	elevation (+), wet precipitation (+)
Particles	0.29	0.51	wet precipitation (-)

\*Sign indicates direction of the relationship to the dependent variable.

throughout the year; downvalley and downslope winds prevail at night and give way to reverse conditions during the day.

Since elevation and wet precipitation are related to each other as well as to deposition, multiple regression was used to separate the effects of the two variables on deposition. Because deposition rates are far from normally distributed, they were log transformed prior to the regression analysis. Thus the analysis involved log deposition rate as the dependent variable and elevation and amount of wet precipitation as independent variables (all annual averages). The regression was forced to accept elevation as the first independent variable so that the residual effect of wet precipitation could be examined after the relation between elevation and wet precipitation had been taken into account. The results of the regression analysis are summarized in Table 5.

#### Deposition Patterns for Major Cations

The annual average deposition rates for calcium, magnesium, sodium, and potassium ions are summarized in the hand-drawn contour maps of Figures 8–11. The deposition rates and concentrations for each station are also given in Tables 6 and 7.

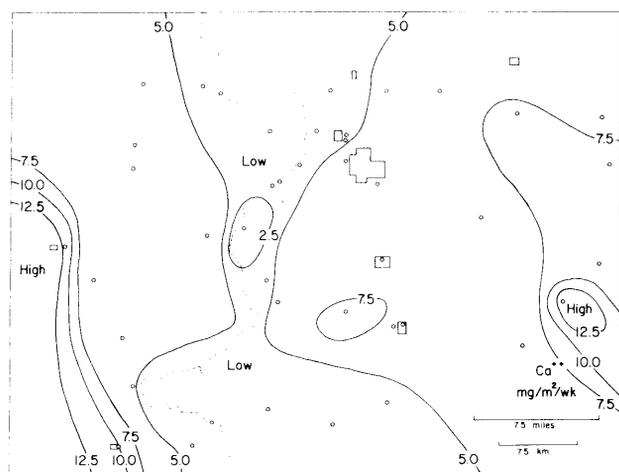


Fig. 8. Calcium deposition.

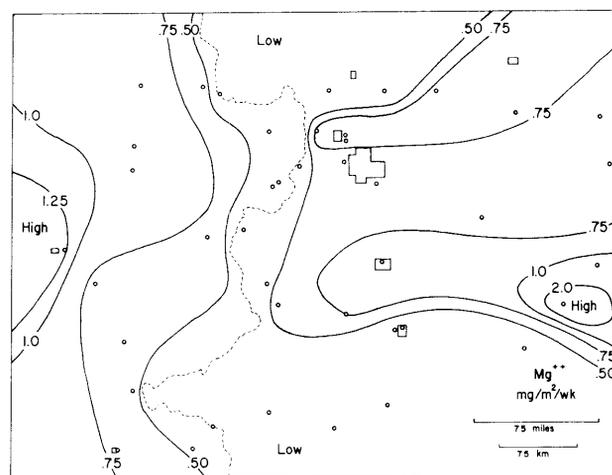


Fig. 9. Magnesium deposition.

Since the patterns for calcium and magnesium are similar, these two ions can be discussed together. For both ions, contour maps suggest relationships with both elevation and wet precipitation; this impression is confirmed by the regression analysis (Table 5). Deposition declines with elevation, but once this effect is taken into account, there is a residual positive relationship of deposition to amount of precipitation. A likely explanation for the elevation effect is that areas of lower elevation are richer sources of soluble calcium and magnesium. Although a number of factors contribute to this, three of the most important are the higher soil reserves of calcium and magnesium, more limited vegetative cover, and shorter period of snow cover at lower elevations. For a given amount of moisture, there is greater drought stress at lower elevations where air temperatures are higher. This results in an elevational vegetation gradient, which has been magnified by grazing and agriculture at low elevations. In addition, longer snow cover at high elevations reduces the exposure of the modest montane terrestrial calcium and magnesium sources. Thus as air containing calcium and magnesium from the lowest elevations begins to flow over the mountains, the loss of aerosols and particles containing these ions by sedimentation, impaction, and removal by moisture is much faster than the addition of calcium and magnesium to the atmosphere from montane sources. This results in an elevation-related reduction of

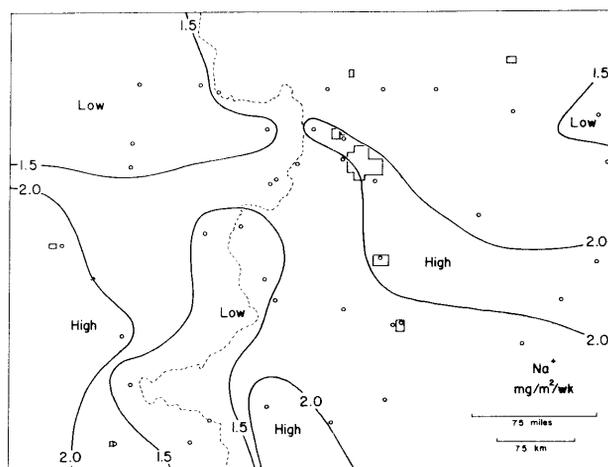


Fig. 10. Sodium deposition.

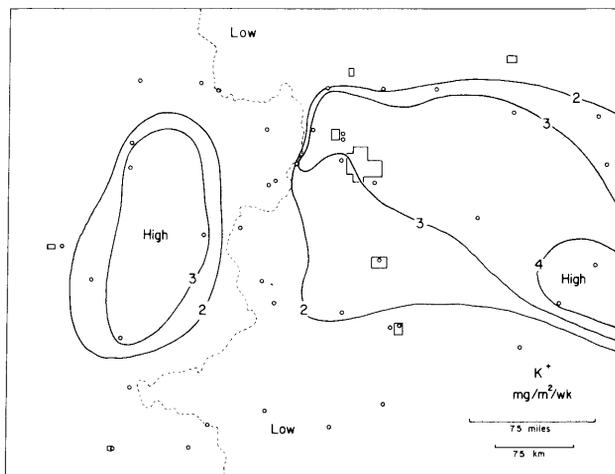


Fig. 11. Potassium deposition.

ture effect caused by the facilitation of deposition by moisture at any elevation.

Sodium shows much more uniform deposition than calcium or magnesium (Figure 10). Confident contouring is difficult because of the uniformity, but the southern mountains and the northwest quarter of the state show lowest deposition; the highest deposition is found in the southwest, around Monte Vista, and in a belt from Denver and Boulder southeast to Eads. There is no obvious relation of deposition to amount of moisture or elevation; this lack of relationship is confirmed by the regression analysis (Table 5).

Potassium presents still a different pattern (Figure 11). Deposition is low over much of the state but is high in west-central and east-central areas. There is a negative relationship with elevation, and no residual relationship with wet precipitation.

*Bicarbonate and Chloride Deposition*

Bicarbonate deposition, shown in Figure 12, can be expected to reflect not only the carbonate sources but also the presence of acidifying materials that convert bicarbonate to

calcium and magnesium deposition for a given amount of wet precipitation. Overlying the elevation effect is separate mois-

TABLE 6. Summary of Deposition Rates by Station

Station Code	Major Cations, mg/m <sup>2</sup> /week				Major Anions, mg/m <sup>2</sup> /week			
	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>=</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
AK	9.57	0.82	1.74	3.05	16.2	4.12	4.30	13.2
AR	6.62	0.50	1.83	1.83	13.4	3.74	3.71	15.5
AS*	6.27	1.43	1.38	4.87	6.94	7.44	1.67	17.7
AU	7.51	0.62	2.68	3.19	16.6	7.02	3.72	8.26
BC*	7.06	0.64	2.31	3.26	8.62	4.37	1.23	13.2
BO	4.41	0.60	1.99	3.59	18.6	4.77	4.17	20.8
BOC	4.95	1.05	1.83	5.30	18.2	3.41	3.30	44.9
BR	8.28	0.62	1.82	2.28	12.7	4.80	4.00	11.2
CC	9.77	0.78	1.78	2.00	16.8	3.87	2.64	6.19
CH	3.07	0.36	1.22	1.79	5.54	8.10	1.14	3.33
CO	5.16	0.94	5.91	3.45	24.1	4.09	3.89	1.16
CR	6.44	0.76	1.38	1.13	15.2	3.09	2.76	5.86
CS	5.45	0.80	2.51	2.51	16.0	3.31	2.85	4.65
CW	8.60	1.03	2.38	4.36	17.2	6.01	4.60	48.0
DE	5.43	0.63	1.86	2.21	13.2	5.27	1.81	13.5
DL*	3.37	0.31	1.72	1.72	16.4	3.40	3.12	2.48
DR	3.45	0.54	1.75	3.31	10.7	4.32	2.48	5.03
DU	10.1	0.68	1.78	1.45	22.2	3.75	2.95	10.1
EA	14.8	2.12	2.58	9.06	23.9	9.76	5.65	40.3
EM	2.58	0.40	1.84	3.22	7.36	4.25	1.48	2.64
FG	3.37	0.31	1.86	1.56	6.56	2.34	1.41	3.59
FR	3.10	0.39	1.55	1.45	7.52	7.41	1.85	3.26
GJ	13.4	1.44	2.03	1.72	18.6	4.13	2.16	28.5
GR	5.27	0.49	1.45	1.31	9.59	3.94	2.41	9.63
HS	2.83	0.33	1.20	1.38	8.75	2.33	1.63	1.27
JR	6.44	0.80	1.84	2.99	15.5	4.26	3.33	11.9
LA	5.87	0.46	1.60	1.83	12.8	3.29	2.74	12.6
LE	2.04	0.28	1.19	1.14	5.03	5.50	1.01	1.90
LI	4.09	0.63	1.77	2.86	10.3	3.60	2.42	8.85
MV	4.19	0.32	2.98	1.61	9.96	2.80	0.78	7.33
PS	3.71	0.51	1.22	1.69	18.5	5.21	2.50	7.50
PU	6.04	0.48	1.87	1.57	12.0	2.67	2.87	6.19
PUI†	26.0	1.52	5.44	3.23	21.8	5.96	4.13	64.5
RE	3.20	0.52	1.69	1.50	25.7	3.98	3.68	0.44
RI	6.01	0.91	1.27	3.87	12.0	4.25	1.92	14.7
SA†	5.65	0.71	4.68	4.74	9.09	2.95	0.27	2.98
SI	5.83	0.66	1.24	0.34	35.8	4.39	2.94	0.77
SS	4.20	0.68	1.41	2.00	16.8	4.41	2.31	3.67
WA	4.91	0.45	1.72	1.69	8.89	3.61	2.05	2.97
WC*	4.44	0.39	1.92	2.11	18.6	4.50	2.83	4.04
WR	5.81	0.45	1.05	2.08	10.5	3.01	3.17	11.2

\*4-6 months.  
†1 month.

TABLE 7. Summary of Composite Average Concentrations

Station Code	Major Cations, µeq/L				Major Anions, µeq/L		
	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>=</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
AK	50	7	8	8	35	12	32
AR	42	5	10	6	36	14	34
AS*	37	14	7	15	17	25	14
AU	50	7	16	11	46	27	36
BC*	56	8	16	13	29	20	14
BO	28	6	11	12	50	17	38
BOC	41	14	13	22	63	16	39
BR	46	6	9	7	30	15	32
CC	72	9	11	8	51	16	27
CH	33	6	11	10	25	49	17
CO	20	6	20	7	39	9	21
CR	50	10	9	5	50	14	31
CS	46	11	19	11	56	16	35
CW	57	11	14	15	47	22	43
DE	83	16	25	17	84	46	40
DL*	14	2	6	4	28	8	18
DR	21	5	9	10	27	15	21
DU	55	6	8	4	51	12	23
EA	89	21	14	28	60	33	49
EM	16	4	10	11	20	15	14
FG	51	8	24	12	41	20	30
FR	23	5	10	6	24	32	20
GJ	178	32	23	12	103	31	41
GR	63	10	15	8	48	27	41
HS	24	5	9	6	31	11	20
JR	52	11	13	12	52	19	39
LA	42	5	10	7	39	13	28
LE	19	4	9	5	19	28	13
LI	38	10	14	14	40	19	32
MV	69	9	43	14	69	26	19
PS	21	5	6	5	44	17	20
PU	46	6	12	6	38	11	31
PUI†	104	10	19	7	36	13	24
RE	9	2	4	2	31	7	15
RI	38	10	7	13	32	15	18
SA†	...	...	...	...	...	...	...
SI	25	5	5	1	63	10	18
SS	30	8	9	7	50	18	24
WA	41	6	13	7	31	17	25
WC*	11	2	4	3	19	6	10
WR	37	3	4	5	20	8	21

\*4-6 months.  
†1 month.

$\text{CO}_2$  and thus reduce the bicarbonate deposition. The richness of carbonate sources can be judged from deposition of divalent cations; the amounts of carbonate-neutralizing acids can be judged from the deposition of strong acid anions ( $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ).

In the western half of the state, there is a gradient from relatively high deposition rates for bicarbonate in the vicinity of Grand Junction toward progressively lower deposition at higher elevations. Evidently there are rich sources of bicarbonate in the western portion of the state, but there is a progressive net removal as air moves from west to east. Over the mountains the bicarbonate deposition is exceedingly low, as it is in the extreme southern part of the state. These are zones of high precipitation acidity, where virtually all weeks of the year are characterized by pH values below the carbon dioxide-bicarbonate equivalence point.

East of the Continental Divide there were two isolated areas of locally high deposition, one in the vicinity of Boulder and the other in the vicinity of Eads and Cheyenne Wells. These have unidentified local carbonate sources. One would expect to see generally high bicarbonate deposition rates to the east of the divide in the plains. With the exception of the locally high deposition already mentioned, however, the bicarbonate deposition rates are relatively low over the entire eastern portion of the state. This reflects the presence of substantial amounts of acidifying materials that convert most of the atmospheric bicarbonate to  $\text{CO}_2$ . Overall there is a strong negative relationship of bicarbonate and elevation but no residual relation to wet precipitation after elevation is accounted for (Table 5).

Chloride deposition, as summarized in Figure 13, bears little resemblance to sodium deposition, nor is it related to elevation or wet precipitation. The highest deposition rates are found in the central montane zone and around Eads. The lack of relation between chloride and sodium deposition reinforces the impression that marine aerosols are not important determinants of atmospheric deposition in Colorado.

#### Sulfate and Nitrate Deposition

Sulfate deposition is summarized in Figure 14. The pattern is very different from that of any of the ions mentioned thus far. The lowest deposition rates are found in the central montane zone, but deposition is also low in the southeastern and

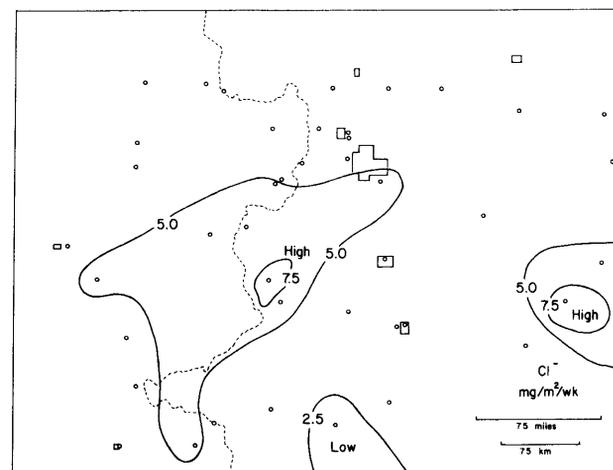


Fig. 13. Chloride deposition.

northeastern plains. In the southwest corner of the state, deposition rates are high, especially at high elevation. Power production facilities in the Four Corners area may augment the deposition rates in this portion of the state. Sulfuric acid originating in the Four Corners area and moving east is removed in transit over the divide, since there is a low deposition zone to the east of the divide.

Sulfate deposition is also high in the northern montane zone downwind from the power plants around Craig. As in the south, the mountains seem to be effective in removing sulfur; the regression analysis shows that wet precipitation, rather than elevation itself, is the determinant of deposition (Table 5). The high deposition rates on the east slope at high elevations may be due to upslope movement from the Front Range urban corridor, as shown for nitric acid at one location [Huebert *et al.*, 1982]. There is a broad zone of moderately high deposition in the east-central zone that appears to reflect the presence of power plants at Denver, Boulder, Colorado Springs, and Pueblo. Eads has especially high deposition, but this is likely to be due to terrestrial  $\text{SO}_4^-$  in view of the high metal cation deposition there.

The connection between power plants and sulfate deposition is speculative. However, our computation of sulfur emission rates on the basis of area has shown that the amount of  $\text{SO}_2$  released by power plants (20.4  $\text{mg}/\text{m}^2/\text{week}$  as  $\text{SO}_4^-$  distributed evenly over the state) is sufficient to account for a

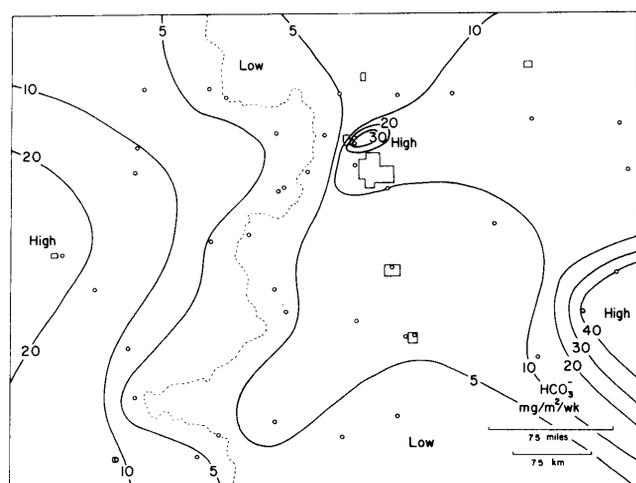


Fig. 12. Bicarbonate deposition.

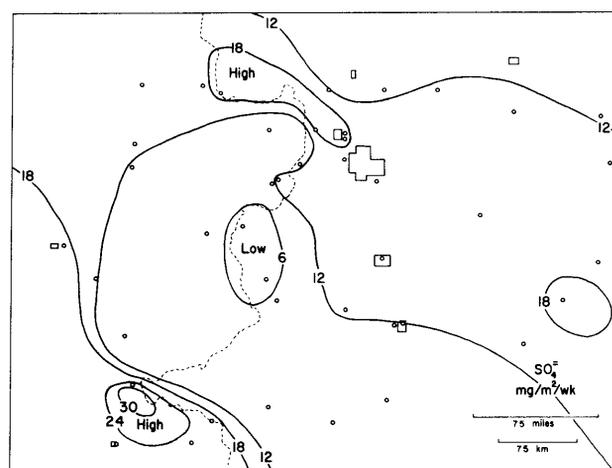


Fig. 14. Sulfate deposition.

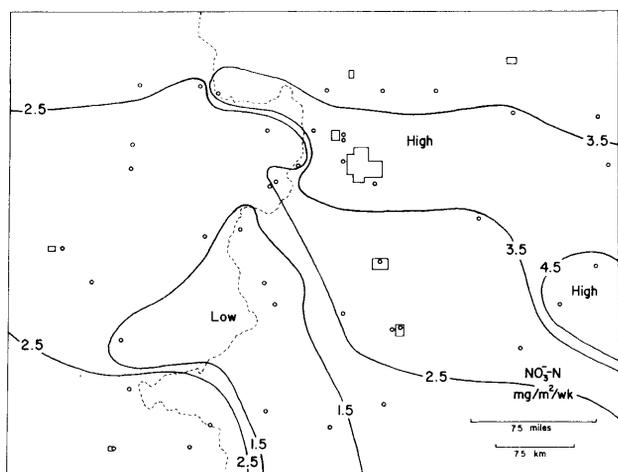


Fig. 15. Nitrate deposition.

large amount of observed deposition (see ranges of values, Figure 14), even if some of the  $SO_4^{=}$  originating from power plants is deposited outside the state. From these comparative numbers and the distribution of sources and prevailing winds, the circumstantial evidence for major power plant effects is strong.

The nitrate deposition diagram (Figure 15) is in some respects similar to the one for sulfate. There is an area of low deposition over the central montane region, and both the southern and northern montane regions are characterized by high deposition. Isolines of high deposition swing east from the urban corridor. In this case the effect of population centers is more pronounced than it is for sulfate, probably because of the large contribution of automobile traffic to nitrate deposition. All of the deposition rates in major population centers are surprisingly similar; they fall in the vicinity of 3 to 5  $mg/m^2/week$  of  $NO_3^- N$ . The area of low sulfate deposition south of Pueblo is also low in nitrate deposition. Just as for sulfate, nitrate deposition is low in the northeast corner of the state and higher in the southwest corner of the state and is especially high in the vicinity of Durango, downwind from Four Corners. Nitrate, like sulfate, has a positive statistical association with amount of wet precipitation and not strictly with elevation (Table 5).

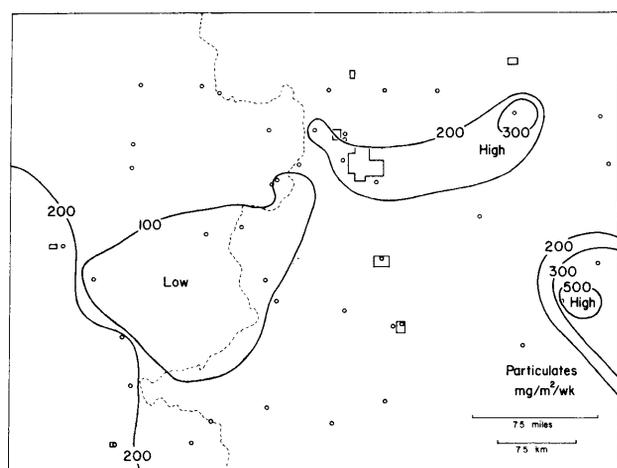


Fig. 16. Particulate deposition.

Particulate Materials

The data on particulate materials are summarized by Figure 16. The data suggest that high particulate deposition at Eads is the cause of exceptionally high anion and cation loadings at this site. Otherwise, the relationship between deposition of particles and deposition of soluble materials is loose at best. There is a zone of low particle deposition over the Continental Divide and extending considerably west of the divide in the central part of the state. Low particle deposition rates are not found exclusively in the mountains, however. As shown by the regression analysis, the only significant relationship is with wet precipitation, not elevation (Table 5), although elevation is close to significance. On the Western Slope low deposition rates are found as far west as Delta, and there are large zones of low to moderate deposition at low elevations both east and west of the divide. The southeastern corner of the state is also quite low in particle deposition. Thus while it might seem safe to assume a priori that the highest particle deposition would occur on the open plains, this is not always the case. East of Denver, deposition tends to follow the same isolines as the

TABLE 8. Variables Related to Acidity

Station Code	Acidity		Acidity, $\mu g/m^2/week$			Rain, mm/yr
	H <sup>+</sup> , $\mu eq/L$	Mean H <sup>+</sup> as pH	Total	Free	% Strong	
AK	2.00	5.70	221	19.1	23	499
AR	9.12	5.04	325	71.0	100	405
AS*	1.09	5.96	293	9.3	32	444
AU	3.31	5.48	153	24.6	72	388
BC*	0.17	6.77	217	1.1	0	326
BO	1.66	5.78	348	13.0	51	405
BOC	2.57	5.59	754	15.6	100	315
BR	1.91	5.72	192	17.1	45	464
CC	7.01	5.15	149	47.4	100	354
CH	8.96	5.05	108	41.7	100	242
CO	10.4	4.98	132	135	84	675
CR	6.53	5.18	147	41.7	100	332
CS	8.07	5.09	123	47.5	98	306
CW	0.82	6.09	789	6.2	20	395
DE	1.17	5.93	224	3.8	62	169
DL*	3.93	5.40	96	48.0	100	635
DR	4.84	5.32	113	40.3	76	433
DU	7.87	5.10	248	71.9	100	475
EA	0.44	6.36	660	3.6	0	431
EM	12.4	4.91	161	97.0	100	406
FG	9.71	5.01	81	32.1	69	172
FR	6.63	5.18	103	43.9	100	344
GJ	0.36	6.45	468	1.4	0	196
GR	0.80	6.10	159	3.4	33	217
HS	11.41	4.94	115	68.1	100	310
JR	1.70	5.77	196	10.5	0	322
LA	0.63	6.20	207	4.4	0	360
LE	8.73	5.06	72	48.1	84	287
LI	2.82	5.55	150	15.2	35	281
MV	2.63	5.58	120	7.9	0	157
PS	9.45	5.03	228	82.7	100	455
PU	2.26	5.65	105	14.8	21	341
PUI†	0.17	6.80	1058	2.1	0	653
RE	17.2	4.77	402	297	100	898
RI	3.53	5.45	252	27.4	41	404
SA†	5.94	5.23	49	0.6	0	...
SI	21.6	4.67	281	256	100	618
SS	13.0	4.89	172	90.6	100	362
WA	6.58	5.18	103	39.2	100	310
WC*	8.06	5.09	194	168	76	1083
WR	0.71	6.15	183	7.7	0	568

\*4-6 months.

†1 month.

sulfate and nitrate deposition, suggesting possible urban sources for a significant proportion of the particles in this area.

### Acidity

Acidity can be quantified in several ways, as shown in Table 8. Because of the complicating effects of the bicarbonate ion, total acidity is not a good indicator of observed (free) acidity, of strong acid anions, or of strong acidity and is therefore of little interest. Average  $pH$ , strong acidity expressed either as deposition rate or as concentration, and observed (free) acidity expressed as deposition rate, concentration, or  $pH$  all are suitable indicators, and all show the same patterns. The most useful general indicator of precipitation acidity is probably the composite average hydrogen ion concentration for the year, as shown in Figure 17, or its  $pH$  equivalent, as shown in Figure 18. Figure 18 also shows for comparison the sum of strong acid anions (nitrate and sulfate).

The background  $pH$  for Colorado is unknown. The  $pH$  5.65, expected of water in equilibrium with  $CO_2$  at sea level, has sometimes been used as a universal background  $pH$  [Galloway *et al.*, 1976b]. Since wet precipitation in the most pristine locations contains substantial amounts of a wide variety of ions, several of which have drastic effects on  $pH$ , it is evident that this universal background reference cannot be taken very literally. Thus it is possible to make general and site-specific objections to the use of such a background  $pH$  [Charlson and Rhode, 1982; Munger and Eisenreich, 1983]. Where there are power plants, population centers, and extensive alteration of the natural vegetative cover, it is unlikely that the regional background will ever be known with certainty. However, in Colorado, the presence of extensive areas of low relief with alkaline soils and low rainfall make it likely that the background  $pH$  of the state as a whole would be above rather than below 5.6. It is possible that the background  $pH$  at highest elevations would be at or below 5.6, but we believe that this is unlikely since some alkaline materials do move upslope, even though they are now neutralized by large amounts of strong acids. It seems safe to conclude that the observed  $pH$  values are considerably lower than one would expect for Colorado and that fossil fuel combustion is implicated, as shown by high deposition rates for nitrate and sulfate over the state, especially downwind from anthropogenic sources.

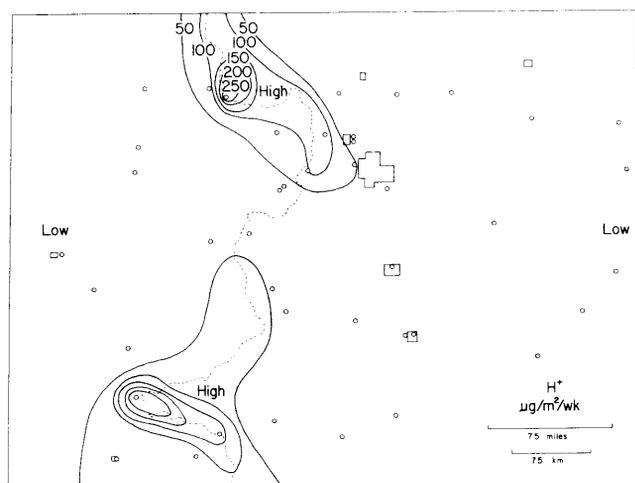


Fig. 17. Hydrogen ion deposition.

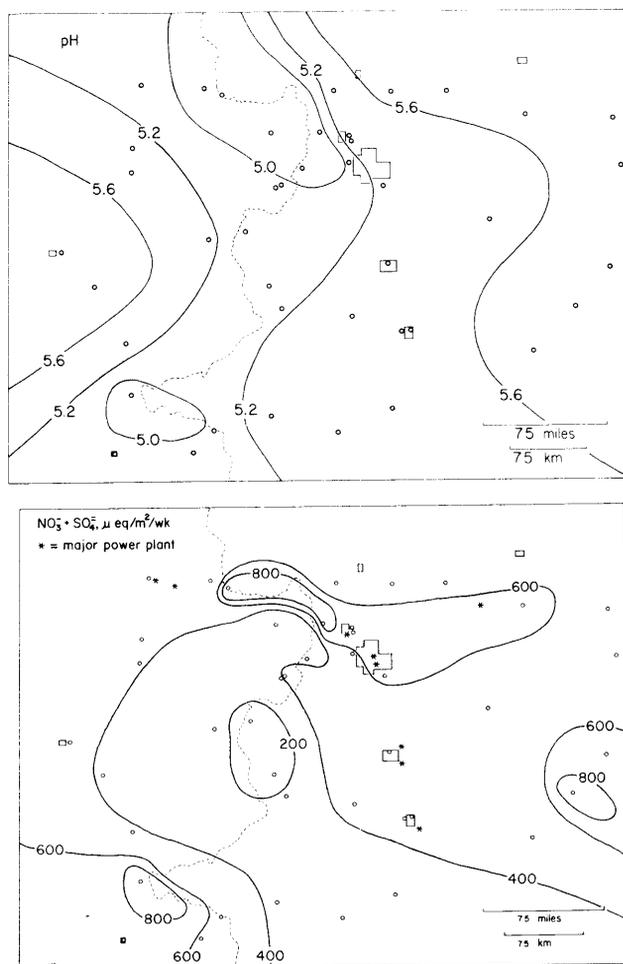


Fig. 18. Contour map of annual average composite hydrogen ion concentration expressed as  $pH$  and, for comparison, contours of the combined deposition of the strong acid anions (nitrate and sulfate).

### CONCLUSIONS

The general patterns of deposition can be understood in terms of three sets of factors: (1) location and potency of sources, (2) transport, and (3) deposition mechanisms. Low elevations are the greatest sources of divalent cations and carbonates. At the same time, because of the location of power plants and urban areas, low elevations are also the greatest sources of strong acids and their anions. Thus at low elevations both alkaline and acid materials are found together in quantity. Important changes occur, however, in the ratio of divalent cations and carbonates to strong acids and their anions as air moves to higher elevations. These changes can be traced to differences in transport and deposition mechanisms. Transport of divalent cations and carbonates by prevailing winds is less efficient than transport of strong acids. Sedimentation plays an important role in the removal of divalent cations and carbonates, as shown by a statistically significant negative relationship of their deposition rates with elevation. Thus even in the absence of significant moisture, net loss of divalent cations and carbonates occurs by sedimentation as air moves upslope. Moisture facilitates deposition, but this is a secondary effect. In contrast, transport of strong acids is more efficient because sedimentation is only a minor deposition mechanism, as shown by the lack of significant relationships

between elevation and strong acid anion deposition. More efficient transport is explained by the origin of strong acids from gaseous precursors ( $\text{NO}_x$ ,  $\text{SO}_2$ ) rather than particles. Moisture is the predominant deposition mechanism for strong acids. Thus as air travels from low to high elevations, divalent cations and carbonates sediment steadily, whereas strong acids remain in the air mass until they are scrubbed out by moisture. This phenomenon accounts for high acidity at high elevations, especially where total wet precipitation is highest.

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