

## Sampling and Chemical Interpretation of Precipitation for Mass Balance Studies

WILLIAM M. LEWIS, JR., AND MICHAEL C. GRANT

*Department of Environmental Population and Organismic Biology, University of Colorado  
Boulder, Colorado 80309*

From an analytical viewpoint, total dry and wet precipitation consists of three fractions: (1) dissolved materials in aqueous precipitation, (2) the water-soluble component of dry precipitation, and (3) the water-insoluble component of either wet or dry precipitation. Methods of precipitation collection and processing greatly affect the separation of these components. A literature survey shows that fraction 3 has typically been ignored and that samplers currently in use lead to a highly variable mixture of the three fractions. Major causes of interpretational ambiguity include (1) variable leaching of dry fallout, (2) particle formation and chemical repartitioning in aqueous precipitation, (3) height, texture, and composition of the collector surfaces, (4) relation of collector surfaces to natural environmental surfaces, (5) contamination by birds, insects, pollen, and organometallic release from local vegetation, (6) sample storage, and (7) failure to analyze insoluble particles. A literature survey also shows that most collectors currently in use are of insufficient size to collect samples large enough to support broad-spectrum analysis on a weekly basis. The minimum satisfactory size of collectors is computed from (1) average rain chemistry, (2) sensitivity of standard chemical tests for chemical species of biological interest, and (3) volume required for each analysis. The computations show that collectors should have an area of at least 1200 cm<sup>2</sup> in regions of average chemistry and as much as 8300 cm<sup>2</sup> in cold climates with minimal aqueous precipitation. A design is given for a collector which combines large size with other desirable features.

### INTRODUCTION

Collection and chemical analysis of precipitation present a large number of technical difficulties. With the increasing application of precipitation analysis to mass balance studies, especially of an ecological nature, methodology has become extremely important in the interpretation of data, yet it has seldom been studied. In the course of designing a scheme of precipitation analysis for nutrient budget studies we surveyed the literature to determine the standard techniques currently in use. The survey disclosed a great variety of collection and analytical methods, some requiring considerably different interpretations than others. We have compiled and organized technical variations here in the hope of saving others a similar effort, and we use this opportunity to emphasize some of the interpretational difficulties that arise from the current variety of methods.

### PRECIPITATION FRACTIONS

The vast majority of precipitation samples have been collected with devices that remain open continuously. Analysis of such samples without any further treatment thus produces a measure of the dissolved material in wet precipitation plus water-soluble materials that have leached from the dry fallout as the sample awaited processing. *Whitehead and Feth* [1964] named this composite the 'bulk precipitation.'

From an analytical viewpoint, precipitation actually consists of three major fractions: (1) dissolved materials in liquid precipitation, (2) the water-soluble portion of dry precipitation, and (3) the water-insoluble components of dry and wet precipitation. We will refer to these below as fractions 1, 2, and 3. Bulk precipitation, as defined by *Whitehead and Feth*, actually includes fractions 1 and 2 but not fraction 3. In fact, fraction 3 is typically filtered out or carried through the analyses without being solubilized; i.e., it is generally neglected. Moreover, attempts at separating fractions 1 and 2 have not been common until recently.

Separation of fractions presents one of the most serious problems in precipitation analysis. A brief examination of three common collection methods will illustrate the nature of the problem.

One of the most common collection devices has been a funnel containing a plug of glass wool in the neck to keep large particulates from passing to the collection vessel [*Gambell and Fisher*, 1966; *Van der Valk*, 1974]. The plug will trap some of the particles and allow others to pass, depending on the way in which it is packed into the funnel. The soluble components of particles trapped in the glass wool will be leached a variable amount with water, depending on the amount and timing of rain that passes through the plug and whether or not the funnel is rinsed when the sample is taken. Particles passing through the plug, on the other hand, will be leached more thoroughly, since they will be immersed if there is any wet precipitation. The use of this method thus blends the fractions in unknown and unpredictable ways. The glass wool also presents a very large surface area which could adsorb dissolved materials.

A second method involves a funnel containing only a coarse screen barrier [*Likens et al.*, 1967] or, in situations where large debris and insects are not a problem, no barrier at all [*Whitehead and Feth*, 1964; *Schindler et al.*, 1974]. The particles reaching the collection bottle are thus leached for a variable amount of time depending on the timing and amount of wet precipitation. The resulting mixture of fractions is thus different from that obtained by the first method but still unpredictable because of the variable leaching time.

A third method relies on the exclusion of moisture in one of a pair of collectors by use of a moisture-sensitive gate or by the exclusion of dry fallout using a similar method. This was also done manually prior to the commercial availability of closing collectors [e.g., *Junge*, 1958; *Junge and Werby*, 1958]. Since the chemistry of wet precipitation can change within a particular precipitation event [*Gorham*, 1958] and since the scavenging efficiency of rain differs considerably between chemical species [*Martens and Harriss*, 1973], the sensitivity of such fraction-

ators is probably quite important. Fieldwork by *Galloway and Likens* [1976] has unfortunately shown that many fractionators are quite unreliable. In addition, the fractionators do not entirely solve the problem of separating fractions 2 and 3. The dry samples must be leached some standard amount of time after collection to release fraction 2. A similar problem actually occurs with the first two methods as well whenever there is no wet precipitation over a collection period.

An additional complication for all three methods arises from the possibility of leaching particulates with acid rather than distilled water. For example, *Elwood and Henderson* [1975] collected dry fallout in a container filled with 0.1 *N* HCl, and *Schindler et al.* [1974] used HCl as a treatment for pooled fractions 1-3 at the time of sample collection. Presumably, the yield of dissolved substances would in these cases be greater than that if distilled water were used. Any additional yield due to the use of mineral acids does not fall within the scope of bulk precipitation as defined by *Whitehead and Feth* [1964] and as commonly conceived in the past by precipitation analysts. Although the acid extraction of dry fallout is reasonable by analogy with standard soil chemistry techniques, the data which it produces will not allow a measure of bulk precipitation chemistry unless a separate water extraction precedes it.

#### MAJOR CAUSES OF INTERPRETATIONAL AMBIGUITY

It is clear that a number of serious methodological problems exist, some of which are general and some more specific to one collection method. The information required either to solve or to justify disregard for these problems can be organized as follows. It will be assumed unless otherwise specified that the purpose of precipitation analysis is to quantify the movement of chemical substances into a watershed or other circumscribed area from outside and to identify the physical and chemical forms of substances as they are transported.

*Leaching of dry fallout.* Since dry fallout contributes half or more of many dissolved substances found in bulk precipitation [*Whitehead and Feth*, 1964; *Elwood and Henderson*, 1975; *Galloway and Likens*, 1976], the effect of leaching on dry fallout is critical. We must know more about the significance of the duration of water extraction. We could already predict on theoretical grounds that the duration of extraction will be important for some substances (e.g., silicates [*Mackenzie and Garrels*, 1965]). The pH will also affect extraction efficiency. Since the pH of bulk precipitation can be quite low [*Cogbill and Likens*, 1974; *Likens and Bormann*, 1974], extraction of dry fallout with distilled water might not be comparable to extraction in wet precipitation. It would be best if fraction 2 were not particularly time or pH sensitive, but this seems unlikely.

*Particle formation and chemical repartitioning in wet precipitation.* Growth of algae and bacteria in the receiving vessel is a potential means by which fractions 1 and 2 can be transferred to fraction 3. Since fraction 3 is typically discarded, the result could be a considerable underestimate of ionic content in bulk precipitation. Some investigators have darkened their receiving vessels to reduce algal growth [*Gambell and Fisher*, 1966]. Although this procedure would not stop bacterial growth, it is simple and may be beneficial. Other investigators have routinely added a preservative to the collector (e.g., chloroform [*Likens et al.*, 1967]). This prevents analysis for dissolved organic carbon, however, which may be of considerable interest. Organic preservatives will also change the extraction properties of the water medium, thus altering the apparent composition of samples.

A related problem is the conversion of ions by biological processes. This particularly applies to the nitrate-nitrite-ammonia complex and to nitrogen, phosphorous, and carbon incorporated into organic compounds. Natural partitioning of inorganic nitrogen between the three major forms in the atmosphere is of great interest [*Eriksson*, 1952, 1960] but cannot be studied without some regard for factors affecting the relative abundance of these species in the collection device.

As it would be ideal to collect precipitation samples without using a preservative, an understanding is needed of the growth of bacteria in standing precipitation samples, particularly of their effect on combined inorganic nitrogen. *Galloway and Likens* [1976] show that in the winter, biological activity over periods as long as 3 weeks is of limited importance to rain chemistry, but the situation may differ in warm weather or in pH ranges higher than those typical of New Hampshire. Repeated use of the same receiving vessel without sterilization invites error, since the biota can build substantial populations under such circumstances.

*Height, texture, and composition of the collector surface.* The analyst will generally want to exclude particles of very local origin from bulk precipitation samples, except when land to water transport of particles is of interest. It is difficult to determine how high the collector must be to avoid substantial contamination of this type, however. A very high collector would be best, but for practical purposes it would be useful to know the minimum acceptable height for a collector. Some experimental studies are needed here or at least some attempt to apply the extensive work on particles per se to precipitation collection methods.

The texture and composition of the collector surface will regulate the amount of dry precipitation that is trapped. *Whitehead and Feth* [1964] found that a rough surface trapped more particles than a smooth surface, but their test must also have been affected by the design of their collectors, which were very gently sloped or not sloped and not shielded. It is known that both deposition and resuspension of particles are extremely variable according to both the surface and the particle properties [*Slinn*, 1976]. Complications for sampling should be minimized by a shield around the collecting surface or a deeply recessed surface to create a dead air space over the collector. Small flat funnels probably do not meet this requirement.

Fluids have occasionally been used to prevent resuspension of particles. *Elwood and Henderson* [1975], for example, used an HCl solution. Absorption of gaseous substances (mainly ammonia, but also possible NO<sub>x</sub>) on an open fluid surface probably invalidates this method. It is generally agreed that wet parts of the system should be sealed from atmospheric contact [*Eriksson*, 1952; *Likens et al.*, 1967] unless the uptake of gases by water is specifically of interest.

Resuspension of dry snow can be especially serious. Some investigators have used heated collectors that melt the snow as it contacts the surface [*Junge and Gustafson*, 1956; *Gambell and Fisher*, 1966]. This would seem almost essential where snow is typically very dry.

*Relation of collector surfaces to natural environmental surfaces.* Even if the collecting surfaces can be standardized in some way, estimations of input to natural surfaces may still be only approximate as long as the relative collection efficiency of surfaces is unknown. Fraction 1 of total precipitation is likely to be the same for all surfaces, whereas fractions 2 and 3 will differ according to the efficiency of a surface in scavenging dry particles from the air. Since fraction 2 may contribute as much as half of the dissolved substances in bulk precipitation [*El-*

wood and Henderson, 1975; Galloway and Likens, 1976], scavenging efficiency will greatly affect total input to natural surfaces. In the future it may well be possible to approximate relative scavenging efficiencies given information on surface type, humidity, wind, and particle size distribution or possibly some simpler subset of these variables. It is already known that vegetated surfaces, particularly forests, remove particles much more effectively than flat surfaces [e.g., Vaughan, 1976]. Hicks [1976] has estimated that a forest removes as much as 10 times as much particulate material as a smooth water surface. This implies that the contributions to ecosystem inputs by fractions 2 and 3 of precipitation will generally be underestimated from precipitation collections by present methodology.

**Birds, pollen, and flying insects.** A bird-proofing device was invented by Egner *et al.* [1955] and has been used extensively with much apparent success. The device consists of a ring of aluminum spikes surrounding the collector. British birds are apparently immune to this trick, however [Allen *et al.*, 1968], so the device must be considered on a site-specific basis.

Pollen has not often been specifically mentioned in the literature as a source of interpretational problems, but it does make a massive local contribution to bulk precipitation at certain times of the year. Local pollen is often released far off the ground and is therefore not excluded by any reasonable elevation of the collector. The only feasible means of excluding local pollen particles from annual measurements would be collection of only wet precipitation during the short pollen season of local trees and use of average figures for dry particle input to complete an estimate of bulk precipitation for this period.

Problems analogous to those posed by pollen arise from release of organometallics from trees, about which very little is presently known [Beaufort *et al.*, 1977].

Insects can be prevented from entering the storage vessel by means of a screen below the collection device, but it is undesirable for the screen to be placed in such a way that insects cannot escape, since dead insects on the screen will be leached by incoming rain. This can be avoided by means of an escape route allowing insects to crawl up the screen and out of the system.

**Storage of samples.** Immediate analysis of samples is ideal but is sometimes impractical or even impossible. Uncertainties of storage are minimized by immediate separation of particle and dissolved phases, however. Hydrochloric acid (1% *N*) is a good preservative for the dissolved fraction, particularly for cations, but may repartition some chemical species (e.g., polyphosphates). Hydrochloric acid also interferes with chloride analysis, so it may be desirable to split the sample and to preserve one part with chloroform or freeze it. Mercury is a good preservative for precipitation (R. Harriss, personal communication, 1977) but creates disposal problems. Storage in plastic now appears to be the norm, although the information on adsorptive properties of plastics is rather limited. Adsorption by plastics is particularly troublesome for phosphate [Riley, 1975] and for nitrate [Grasshof, 1976].

The only studies specifically relevant to precipitation collection are those of Galloway and Likens [1976], who demonstrated significant inorganic contamination by glass and organic contamination or phosphorus adsorption by plastic. Galloway and Likens cleaned their glass containers with chromic acid between samples, however. This etches and thus reactivates the glass surface, which probably aggravates contamination. We prefer thorough rinsing followed by dry sterilization at 150°C.

Very long term storage of samples in plastic with chloroform may be unreliable due to the high vapor pressure of chloroform, which tends to escape through the typically imperfect seal of a plastic cap. Frozen samples must be thoroughly warmed for silica analysis because of apparent polymer formation in very cold freshwater samples [Kobayashi, 1966]. Galloway and Likens [1976] have shown that acidic samples store quite well for most purposes, but a critical pH has not yet been established.

Any stored sample offers fewer analytical possibilities than a fresh sample. In particular, the ratios of various forms of an element must be regarded as suspect as well as the absolute concentrations of any element present in small amounts. More specific information on particular storage techniques would obviously be of great value in planning a storage strategy.

**Analysis of the particle fraction.** It is very difficult to guess how large fraction 3 would be as a proportion of fractions 1 and 2, since fraction 3 has seldom been studied. It is possible that fraction 3 will prove to be quite refractory, in which case its potential yield of major ions or essential plant nutrients could be negligible. The water-insoluble chemical components of the particles could thus be excluded from nutrient budgets on the grounds that they are not labile. There are presently no grounds for such an assumption, however. Extremely fine particles might weather at a rather rapid rate on the soil surface and thus liberate ions, and it could also be argued that the chemical constituents should be considered an input to the system whether they become available immediately or not. The only really satisfactory solution at present is routine analysis of insoluble material in addition to the traditional analysis for water-soluble components.

#### MINIMUM SIZE FOR COLLECTORS

Although the size of the collector determines the sample size, which in turn limits the analytical possibilities, very little consideration of this matter appears in the literature. Many of the funnel collectors now in wide use are only a few centimeters in diameter. Our own experience shows that if a reasonably comprehensive chemical breakdown is done on a precipitation sample, the amount of dilution required for a small sample is often so great as to cause analytical problems, especially if the collections are made weekly.

Table 1 lists the major chemical components that are most likely to be included in any comprehensive study of precipitation, particularly a study with ecological emphasis, and the required volume for analysis. Additional items might be added in certain instances (e.g., Fe, I). Specific interest in trace materials would of course require special techniques not covered here. The methods listed in the table are the most sensitive standard techniques now in use. Special techniques that require unusual instrumentation (e.g., neutron activation) are not considered here.

In addition to the volumes listed in Table 1 a small volume of the sample may be needed for determination of pH and conductance. The volumes in the list could be adjusted downward in some cases by careful planning, but it is assumed that special precautions are not desirable. Most of the wet chemical methods require 100 ml for duplicates or for duplicates plus special blanks. Concentrations of some constituents will be such that a 10-cm spectrophotometer cell will be required to read absorbances, and in such cases it is unrealistic to use less than 50 ml per replicate. The volumes total 1110 ml, which could be considered the minimum volume for analysis, so any

TABLE I. List of Bulk Precipitation Constituents Likely to Be of Ecological Interest Together With the Most Sensitive Common Methods of Analysis

Component	Method	Reference	Minimum Volume, <sup>a</sup> ml	Analytical Limit, <sup>b</sup> µg/l	Amount Required, <sup>c</sup> µg	Average Amount in Bulk Precipitation, <sup>d</sup> kg/ha/yr	Collection Area Required, <sup>e</sup> cm <sup>2</sup>	Minimum Amount in Bulk Precipitation, <sup>f</sup> kg/ha/yr	Corresponding Collection Area Required, <sup>g</sup> cm <sup>2</sup>
Ca	atomic absorption		15	50	60	7.8	40.0	1.7	183.5
Mg	atomic absorption		15	10	12	3.4	18.4	0.4	156.0
Na	atomic absorption		15	10	12	9.9	6.30	1.1	56.7
K	atomic absorption		15	100	120	2.0	312.0	0.3	2080.0
HCO <sub>3</sub>	acid titration	<i>Golterman [1969]</i>	100	1000	1200	53.6	116.4	21.8	286.2
Cl	argentometric	<i>American Public Health Association [1975]</i>	100	500	600	5.0	624.0	3.5	891.0
SO <sub>4</sub>	barium precipitation	<i>Golterman [1969]</i>	100	1000	1200	23.8	262.2	1.6	3900.0
NH <sub>3</sub> -N	phenylhypochlorite	<i>Solorzano [1969]</i>	100	5	6	2.1	14.9	0.05	624.0
NO <sub>3</sub> -N	reduction to NO <sub>2</sub> , azo dye	<i>Bendschneider and Robinson [1952]</i>	100	3	3.6	2.1	8.91	0.10	187.2
		<i>Wood et al. [1967]</i>							
Dissolved organic N	UV combustion	<i>Armstrong and Tibbets [1968]</i>	200	8	9.6	0.6	83.2	0.11	453.8
		<i>Manny et al. [1971]</i>							
PO <sub>4</sub> -P	molybdate	<i>Murphy and Riley [1962]</i>	100	1	1.2	0.10	62.4	0.003	2080.0
Dissolved organic P	UV combustion	<i>Armstrong and Tibbets [1968]</i>	100	2	2.4	0.10	124.8	0.003	4160.0
		<i>Manny et al. [1971]</i>							
Dissolved organic C	gas chromatography	<i>Menzel and Vaccaro [1964]</i>	50	100	120	15.0	41.6		
Si	molybdenum	<i>Golterman [1969]</i>	100	100	120	2.0	312.0	0.039	307.7

<sup>a</sup>Minimum volume required for analysis.

<sup>b</sup>Lower analytical limit for the test.

<sup>c</sup>Total amount required to meet the analytical limit in a volume of 1.2 l, the minimum volume to do all tests.

<sup>d</sup>Approximate average amount of each constituent in bulk precipitation over land.

<sup>e</sup>Minimum collection area required to yield necessary amount for analysis on a weekly basis, assuming that the average input is equally divided between weeks.

<sup>f</sup>Approximate minimum amount of each constituent likely to be found in bulk precipitation.

<sup>g</sup>Corresponding minimum collection area required to yield necessary amount for weekly analysis, assuming dilution to 1.2 l (g).

sample not reaching this volume would have to be diluted. Obviously, samples from small collectors will almost always have to be diluted.

Table I also gives the approximate lower limit for reliable routine analysis of each constituent using the indicated techniques. From the total volume required for analysis (1.2 l) and the analytical limits, it is possible to calculate the weight of each substance required to complete a successful analysis (e.g., for calcium,  $50 \mu\text{g/l} \times 1.2 \text{ l} = 60 \mu\text{g}$  is required). The results of these calculations are given in Table I. These figures provide the means for computation of the minimum required collection surface if the delivery rate of each constituent per unit time can be approximated.

Some of the constituents of precipitation listed in Table I have been studied extensively, and others scarcely at all. In order to obtain an average value for each constituent in the list we selected a group of comprehensive studies from which a list of representative values could be compiled. All of these references give analyses of bulk precipitation as defined by *Whitehead and Feth [1964]*. Some excellent studies which intentionally excluded chemical fraction 2 were omitted because they are not comparable. References that were used include work by *Eriksson [1952, 1960]*, *Whitehead and Feth [1964]*, *Gambell and Fisher [1966]*, *Fisher [1968]*, *Allen et al. [1968]*, *Wells et al. [1972]*, *Elwood and Henderson [1975]*, *Lemee [1974]*, *Schindler et al. [1974]*, and *Likens et al. [1976]*. None of the references contained data on all the constituents listed in

the table. The work by *Likens et al.* covers the greatest time span, and that of *Schindler et al.* is chemically the most comprehensive. An average was obtained for each constituent from these references in terms of kilograms per hectare per year. These averages are assumed to be near the average values for bulk precipitation over land. The averages for dissolved organic N and P, Si, and bicarbonate are based on many fewer data than those for other items in the list, since only one or two references included measurements for these. The value for dissolved organic carbon is based on our own unpublished data for a mountain watershed in Boulder County, Colorado, since none of the references contained measurements of this constituent.

Table I also gives the minimum yield of each constituent from the references cited above. In all cases these minima come from the data of either *Likens et al.* or *Schindler et al.* The data of *Schindler et al.* must be very near the absolute minimum over land for most constituents, since the low amount of wet precipitation and the long periods during which the ground is frozen and snow covered in the study area combine to limit terrestrial sources.

If the annual input of various constituents of precipitation is assumed to be evenly distributed through time and collections are assumed to be done weekly, then it is possible to calculate the minimum collection surface needed to produce the amounts of each substance required for analysis. Table I shows the results of such calculations for average bulk precipi-

tation and for bulk precipitation containing probable minimum amounts of all substances. Collection at intervals shorter than 1 week would make these collection areas proportionately larger or, at intervals longer than 1 week, proportionately smaller. The assumption of equal distribution of input over time is of course merely for calculation of an average figure. The minimum chemical input, except in very dusty areas, will typically occur on weeks with no rain, when the content of bulk precipitation is entirely due to chemical fraction 2. Fraction 2 apparently contains roughly half of the water-soluble chemical constituents in moist areas [Elwood and Henderson, 1975; Kluesener and Lee, 1974; Galloway and Likens, 1976]. In dry areas the ratio of fraction 2 to fraction 1 may be greater [Whitehead and Feth, 1964]. The minimum collection can thus be approximately doubled to account safely for weeks of the year with no wet precipitation input.

Table 1 shows that in an area of average bulk precipitation input the collector surface will have to exceed 1200 cm<sup>2</sup> (2 × 624) to allow satisfactory analysis every week for every constituent listed in the table. In areas of absolute minimum bulk precipitation, typically northern wilderness with low annual wet precipitation, the collection area will have to exceed 8300 cm<sup>2</sup> (2 × 4160). Square collectors will therefore have to be between 35 and 95 cm on a side, depending on location, the lower end of this spectrum being satisfactory in most instances. Such dimensions far exceed those of the usual collectors currently in use.

#### NUMBER OF COLLECTORS

It is customary to measure amount of wet precipitation at a network of stations, even in a relatively small watershed, since the amount of precipitation per unit area is highly variable, particularly for individual storms. Such networks are highly impractical for chemical studies unless samples are pooled. The minimum possible number of stations required to represent an area in terms of chemical input is therefore of great interest. Preliminary indications suggest that weekly chemical input is not nearly so variable as amount of wet precipitation. Likens *et al.* [1967] found no consequential difference between paired stations in the same watershed. Our unpublished data from the watershed of Como Creek, Colorado, show the same result. Figure 1 shows NO<sub>3</sub>-N in bulk precipitation weekly over a 2-year period on Como Creek at two stations 1 km apart and differing in altitude by 100 m. Although more com-

prehensive studies are still required, it appears that even one station may give meaningful chemical data for a single watershed of small to moderate size. Paired stations of course offer protection against gross error at any single station.

#### DESIGN FOR A PRECIPITATION COLLECTOR

We have designed and used a precipitation collector that attempts to minimize some of the problems that have been mentioned here. Figure 2 shows the design, which incorporates a number of separate ideas from the literature.

The outside box is constructed of  $\frac{1}{2}$ -inch marine plywood and is sealed to be waterproof. All interior surfaces except the top are covered with 1-inch styrofoam glued to the plywood. A door, mounted hinges down, is cut large enough to allow easy removal of vessels inside the box. Three 200-W incandescent light bulbs are mounted on the inside walls to the left side of and opposite the door. Electrical receptacles are mounted on strips of 1 × 4 inch firring screwed to the plywood. These bulbs are controlled by a common 110-V thermostat set to keep the temperature nominally at 40°F. The bulbs supply sufficient heat down to at least -20°C. Snow melts on contact with the collector surface.

The top of the collector consists of two  $\frac{1}{2}$ -inch Plexiglas pieces. The uppermost piece consists of a horizontal square-shaped flange which extends beyond the plywood box along its outside edges and defines the collection opening along its inside edges. This horizontal flange is fastened to the plywood with stainless steel screws. Rubber weather stripping between the plywood and Plexiglas seals against water. Additionally, there are four 4-inch vertical flanges along the inside edges of this piece which extend below the upper edge of the Plexiglas funnel. This recess helps retain hail, which otherwise tends to bounce out. The second part of the collector top is a Plexiglas funnel of pyramidal shape supported by wooden mounts inside the collection box. The funnel is constructed of four truncated isosceles triangles whose base and apex are beveled at 60° and whose legs are beveled at 33°. These four triangles are glued together to form the main receiving funnel.

We leached Plexiglas with distilled water in the laboratory and found its yield of the substances in Table 1 to be negligible compared to the amounts found in precipitation.

The large Plexiglas funnel empties into a standard laboratory polypropylene funnel with coiled surgical rubber tubing leading into a 2-l hard glass receiving vessel. The poly-

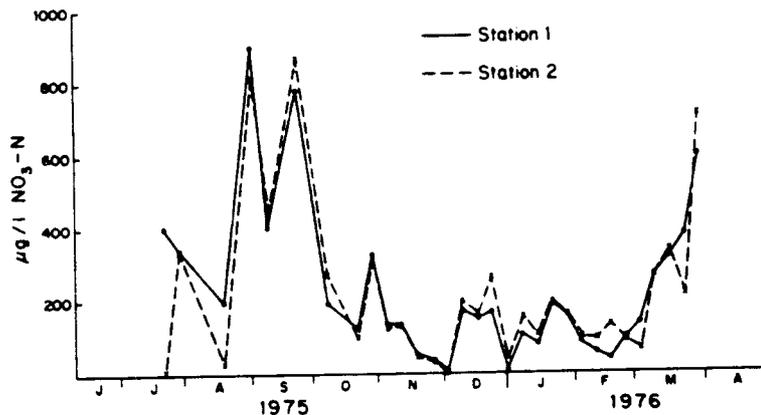


Fig. 1. Concentration of NO<sub>3</sub>-N in bulk precipitation at weekly intervals for paired stations in the Como Creek Watershed, Boulder County, Colorado. Stations are 1 km apart and 100 m different in elevation.

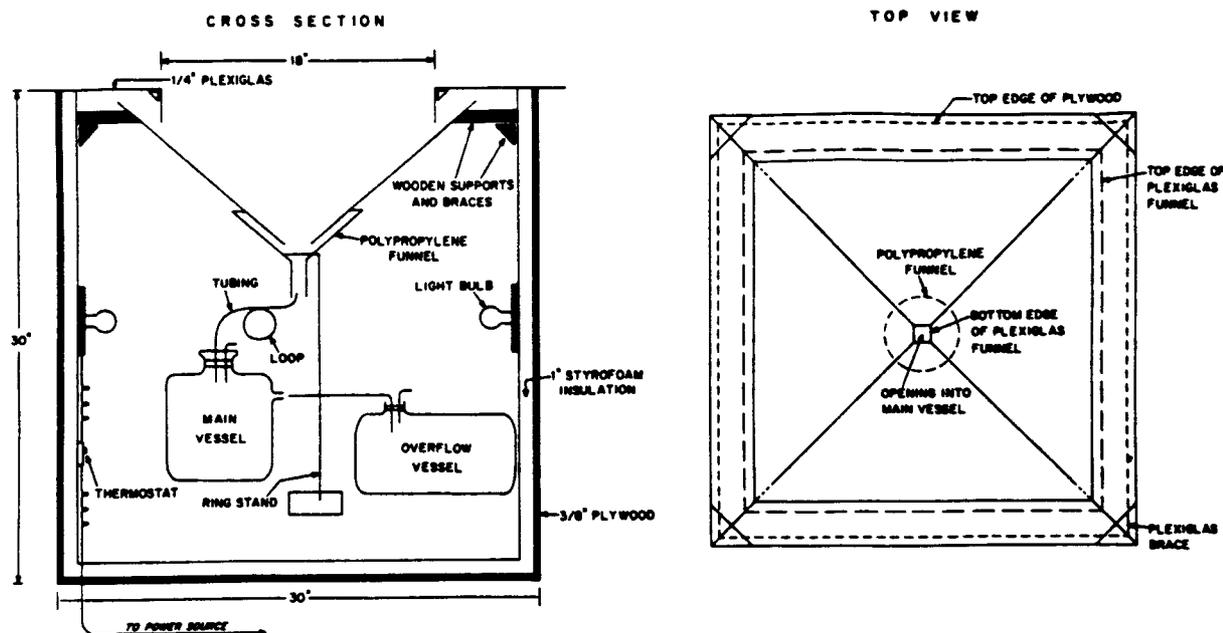


Fig. 2. Schematic diagram of bulk precipitation collector (see text).

propylene funnel is lined with a nylon screen (1-mm mesh) extending to the top of the funnel so that insects can climb over the edges. The tubing coils supply the 'vapor barrier' recommended by Likens *et al.* [1967]. The collection vessel is masked with foil to prevent photosynthesis and is replaced weekly when the sample is collected. The vessel is equipped with a side port and tubing leading to an overflow container that accommodates heavy rains. The overflow container consists of a collapsible plastic carboy. Both the main storage container and the overflow container are vented. Although it is possible to put vapor barriers on the vents as well as the intake [Likens *et al.*, 1967], we do not believe that this is necessary.

The collector shown in Figure 2 provides for a collecting area of 2025 cm<sup>2</sup>, a comfortable margin beyond minimum requirements in regions of near-average annual chemical input (Table 1). The collector is mounted 3 m from the ground surface on a wooden tower secured by guy wires.

The capture efficiency of the bulk collector for aqueous precipitation is essentially identical to that of a standard recording rain gauge with shield. A well-shielded standard collecting gauge operated by the University of Colorado Mountain Research Station east of our sites yielded estimates of 685 and 673 mm of water equivalent for 1976 and 1977, respectively, while our collectors gave estimates of 692 and 625 mm for the same years.

#### CONCLUSIONS

The study of precipitation chemistry is obviously subject to a large number of methodological difficulties, some of which can be of sufficient importance to affect interpretation of mass balance data. Remedies which seem clear at present include use of large collectors, recognition of the potential significance of all precipitation fractions, and analysis of fresh samples. No reliable guidelines are available for solution of other problems connected with collector height, sampling network size, and particle decomposition in water solution. In view of the increasing interest in and importance of precipitation chemistry, these problems should be systematically investigated.

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