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The collection of precipitation for chemical analysis

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ABSTRACT

This paper is one of a series of publications on the collection and chemical analysis of precipitation. While the first paper presented the results from an intercalibration of 10 different designs of precipitation collectors (Galloway and Likens, 1976), this paper presents results of experiments on the collection efficiency of collectors, preservation of samples, monthly variation of wet and dry deposition, sample storage, length of sampling period, choice of collector location and sources of variability in precipitation data. The primary conclusions are that dry fallout should usually be excluded from rain and snow samples, sampling should be on an event basis, all biocides tested have some detrimental effect on sample composition, and that the major sources of variability in precipitation data are due to sampling errors and choice of collector location.

1. Introduction

The chemical investigation of precipitation (rain and snow) is not a recent phenomenon. For over a century (Dalton, 1825) researchers have been sampling precipitation to measure its chemical composition. With this history of experience, it would be natural to assume that documented and standardized procedures for sampling and analysis would be in existence. While it is true that these techniques are documented (the growing volume of published literature attests to this), the techniques are certainly not standardized and in many cases are not well conceived.

The question of how to sample precipitation for chemical analysis is actually a series of questions. It begins with the basic ones—How do you collect a sample? What component of precipitation do you need to measure to answer your research hypothesis?—and ends with—What are the constraints on the interpretation of precipitation chemistry data?

Earlier, we reported results from an intercalibration of 22 precipitation collectors of 10 different designs (Galloway and Likens, 1976). This report presents the results of experiments on collection efficiency of collectors, preservation of samples, analytical techniques, sample storage, data variability, etc.

2. Components of precipitation

In a general sense, precipitation has only one component, which is defined as anything wet that falls out of the atmosphere. However, there is also a dry component that is transferred from the atmosphere to ground surfaces. This is termed dry deposition and has three subcomponents.

Dry fallout: Particles that are affected by gravity to such a degree that they fall on earth surfaces (vegetation, water, soils). Particles are necessarily large (usually >2 μm diameter) and are usually derived from soils, plant debris or condensed aerosols.

Impacted aerosols: Smaller particles that are impacted onto earth surfaces.

Adsorbed gases: Gases that are adsorbed on or by earth surfaces.

Due to the difficulties in sampling atmospheric aerosols and the need to estimate a depositional velocity, this investigation considered only wet precipitation, bulk precipitation and dry fallout. Wet precipitation is defined as the material deposited during rain and snow events only. Bulk precipitation is defined as a combination of wet precipitation and dry fallout (Whitehead and Feth, 1964).

3. Collector types

There are three generic types of precipitation collectors commonly used in precipitation chemistry studies—bulk (collects precipitation and dry fallout in the same container), wet/dry (automated collectors that collect precipitation separately from dry fallout) and wet (collects precipitation only).

Bulk precipitation collectors vary in design from the very simple, consisting of an open container, to the complex, equipped with vapor traps, overflow bottles, bird discouragers and insect filters. Wet and wet/dry precipitation collectors are automated with the basic components being a collection vessel with a movable lid, connected to a motor which is activated during periods of rain or snow.

There are currently several designs of bulk, wet and wet/dry collectors in use. Some 22 collectors of 10 different designs were tested for reliability in an earlier study (Galloway and Likens, 1976) and the results are presented in Table 1. The relative rating reflects performance under field conditions over a 2-year period.

4. Efficiency of precipitation collectors

The ideal precipitation collector should representatively sample precipitation relative to precipitation composition (mg/liter) and ecosystem loading (mg/m^2). However, it is difficult to imagine that a collector, with a finite opening located above the ground will collect precipitation identically as an earth surface. This would seem to be especially true during periods of wind or light precipitation.

Precipitation amount in the United States is measured with standard rain gauges by the National Weather Service, NOAA. To relate precipitation composition to elemental deposition, it is necessary to know how efficiently a precipitation collector samples precipitation amount relative to a standard rain gauge. Since the differences between the two are ones of design and the fact that the rain gauge is surrounded by a wind shield to

Table 1. *A qualitative rating of precipitation collectors*

Collector	Type	Manufacturer	Qualitative rating*
Hubbard Brook Rain	Bulk†	Hubbard Brook Ecosystem Study	4
Hubbard Brook Snow	Bulk	Hubbard Brook Ecosystem Study	4
Bulk Glass	Bulk	This laboratory	2
Misco	Wet‡	Misco Scientific	1
Wong	Wet	Wong Scientific	3
ERNI	Wet	ERNI & Co.	1
Parelco Oy	Wet/Dry§	Parelco Oy, Finland	3
HASL	Wet/Dry	Health and Safety Laboratory, U.S. Energy Research and Development Administration	4
ISWS	Wet/Dry	Illinois State Water Survey	3

* This qualitative rating is based on a scale from 0–5. A rating of 5 indicates that the collector has functioned well during this two-year investigation on collector reliability. A rating of 4 means that minor problems were encountered but that the collector is a suitable instrument for precipitation collection. A 3 rating indicates marginal suitability and ratings of 2 or 1 indicate the collector is not adequate for the collection of precipitation for chemical analysis. For details on the specific problems with each collector, refer to Galloway and Likens (1976).

† A Bulk collector is open to the atmosphere at all times and collects rain, snow and dry fallout.

‡ A Wet collector is an automatic collector open to the atmosphere only when it rains or snows.

§ A Wet/Dry collector is an electrically powered collector that samples precipitation and dry fallout in separate containers.

Table 2. *The effect of a wind shield on collection efficiency* relative to a standard rain gauge*

Collector	N	Without a wind shield	With a wind shield
Hubbard Brook—Summer	18 events	0.93 ± 0.24	0.97 ± 0.20
Hubbard Brook—Winter	14 events	0.71 ± 0.24	0.78 ± 0.17

* The values represent the following function:

$$\text{Efficiency} = \frac{1}{n}\sum_{i}^{n} \frac{\text{precipitation deposition as determined by a bulk precipitation collector}}{\text{precipitation deposition as determined by a standard rain gauge}} \pm \text{one standard deviation}$$

where $i = n$ precipitation events.

reduce wind effects, it is possible that any differences in collection efficiency can be eliminated by surrounding the collector with a wind shield.

To determine the efficiency of collection relative to a standard rain gauge, the following experimental setup was devised: Two bulk precipitation collectors were placed within 5 m of each other at the National Weather Service station in Ithaca; one had a wind shield and the other did not. For a period of 11 months, both bulk collectors were sampled on an event basis (32 separate storms). The precipitation amount as determined by these two bulk collectors was compared with that measured by a standard rain gauge located 25 m from the bulk collectors. The collection efficiency of these precipitation collectors was less than that of a standard rain gauge (Table 2). The collectors were less efficient in the winter than the summer. The effect on collector efficiency of adding a wind shield to the collection assembly was not significant at the 10% level.

While the wind shield had no effect on the average amount of precipitation collected during the test period (Table 2), seven events out of the 36 had a more efficient collection of precipitation in the collectors with wind shield. (The criterion for more efficient collection was arbitrarily taken as whenever the wind-shield-equipped collector had greater than 9.9% more volume than in the collector without the wind shield.) To determine if this greater efficiency in precipitation collection had a corresponding effect on precipitation composition the following calculation was performed. For every event the ratio between the concentration of the chemical parameter from the wind-shield-equipped collector and the collector without a wind shield was taken. The events were divided into two groups using the criterion for collection efficiency stated above. The mean and standard deviation of each group was calculated and a *t*-test performed to indicate if there was a statistical difference (hence an effect of the wind shield on precipitation composition) between the two groups. There were no significant differences found for any chemical parameter.

The fact that a wind shield does not consistently improve the collection efficiency of a precipitation collector relative to a standard rain gauge is somewhat surprising. Possible reasons are due to the design differences between the precipitation collectors and the standard rain gauge and the size of the collector relative to the wind shield.

5. The influence of dry fallout on rain and snow composition

Bulk precipitation has been defined (Whitehead and Feth, 1964) as the material that is deposited into a collector continually open to the atmosphere. A bulk collector is the least expensive and has been used widely in past investigations of precipitation chemistry. There can be, however, severe limitations imposed upon these data due to a chemical influence of dry fallout on the chemistry of rain and snow within the collector. To determine the magnitude of this influence, wet and bulk precipitation and dry fallout were collected on an event basis for 2 years at Ithaca, New York. From the composition data, weighted monthly means (weighted by the amount of precipitation collected) were calculated for wet, bulk and dry fallout deposition (deposition is defined as grams of material deposited per square meter). The following ratio was used to indicate the influence of dry fallout on the chemistry of rain and snow.

$$\text{Bulk/Wet} = R = \frac{\text{Weighted Monthly Deposition Based Upon Bulk Collectión}}{\text{Weighted Monthly Deposition Based Upon Wet Collection}}$$

If $R > 1$, dry fallout of the element has occurred or material was lost from the wet collector.

If $R = 1$, no dry fallout has occurred.

If $R < 1$, dry fallout has reduced the measurable component of the element or material was lost from the bulk collector.

Elements common in soils—K, Na, Ca and Mg—are the most prevalent in dry fallout, and thus are most enhanced in bulk precipitation (Fig. 1). Presumably this is caused by soil particles being blown into the atmosphere by wind action. Other chemicals—NO_3, NH_4 and SO_4—are less abundant in dry fallout and have a smaller enhancement on rain and snow chemistry (Fig. 2). The only parameter that shows a consistently negative influence due to dry fallout is hydrogen ion (Fig. 2). It appears that the dry fallout has a small

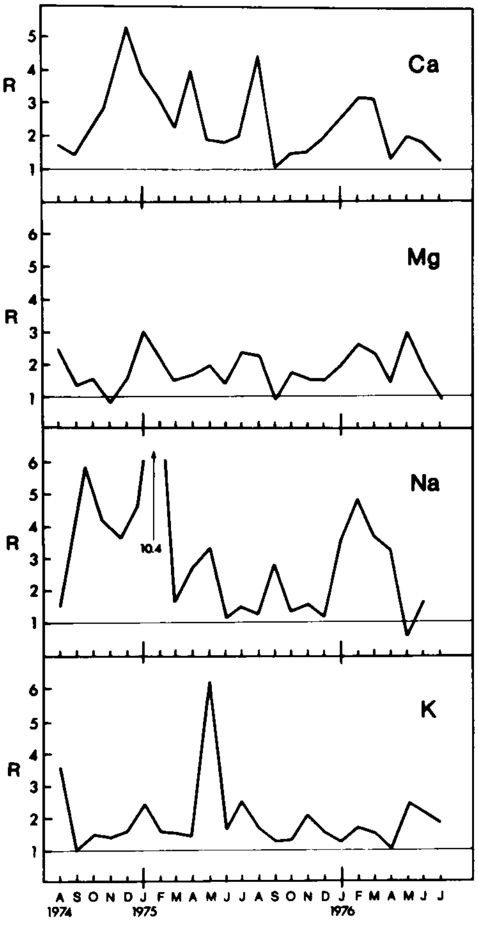

Fig. 1. The influence of dry fallout on the K, Na, Mg and Ca concentration in precipitation. The ratio R, defined in the text, is plotted as a function of the month.

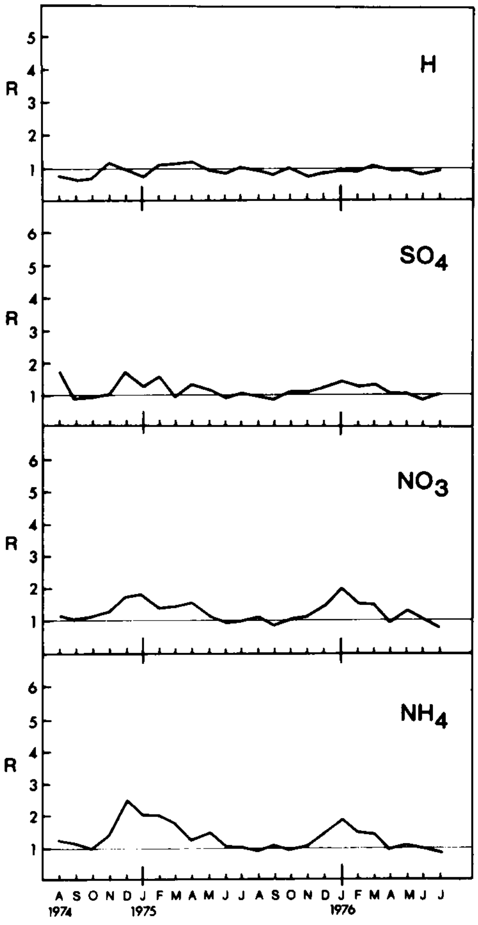

Fig. 2. The influence of dry fallout on the H, NO_3, NH_4 and SO_4 concentration in precipitation. The ratio R, defined in the text, is plotted as a function of the month.

neutralizing effect on the hydrogen ion concentration of rain and snow. In most cases, there is a definite seasonal trend with appreciably more dry fallout in the winter months than in the summer. This is shown most clearly for NH_4, SO_4, NO_3 and Na.

Another way to determine the magnitude of dry fallout is to collect it in a separate collector. Once the deposition of dry fallout is known, it can be added to the deposition value for wet only and a total deposition computed (Galloway and Likens, 1976).

The main conclusion of the influence of dry fallout on the composition of bulk rain and snow is that the inclusion of dry fallout introduces a complexity in the investigation of precipitation chemistry. It has a definite effect on the measured composition of rain and snow which may be seasonal and varies with each element.

Therefore, we believe that dry fallout should be excluded from rain and snow samples unless information on bulk deposition only is required.

6. Sampling period

To test the length of time that samples can remain in the field, seven field experiments were performed. All the experiments had the same design: Identical bulk collectors, in sets of two, were placed in the field. One collector (designated "event"[1]) was sampled on an event basis for a series of 3–8 storms depending on the experiment. The other collector (designated "composite") was not sampled until the end of each experiment. Therefore this collector contained a composited sample of all events within the period. Both collectors were open to the atmosphere at all times, therefore both collected dry deposition as well as precipitation. If there were no effects due to the length of sampling time, then the sum of the amounts of an element in the samples from the event collector should equal the amount of the element in the sample from the composite collector within the limits of variability due to two adjacent collectors. The results of the experiments (Table 3) indicate that a large degree of variability is introduced in the data. Included in this variability of event versus period sampling is the natural variability between two adjacent collectors. An analysis of variance shows that the variance introduced by lengthened sampling time is much greater (3–100 times, depending on element) than the variance caused by adjacent collectors (Table 4). There are a number of factors associated with period sampling that can cause this large variability. Primary ones are an increased probability for contamination, evaporation and chemical or biological changes. For example, the large value of R for volume during the first sampling period (Table 3) is due to evaporation of the composite sample.

7. Sample preservation

A factor related to sampling period is sample preservation in the field and the laboratory. A standard method is to add biocide to the collection bottle. This, however, has some disadvantages because of sample contamination by the biocide and biocide interference with analytical techniques.

To investigate this, two general types of biocides, additive and manipulative, were tested. Additive biocides are reagents added to the sampling bottle, which can be used to preserve samples in the field. Manipulative "biocides" are techniques to preserve samples, without the addition of reagents, such as freezing, refrigeration and dark storage. These techniques cannot be adapted easily for use in the field but can be used conveniently in the laboratory. The additive biocides tested were selected because of their availability and previous use in published precipitation chemistry studies.

A large volume of precipitation was thoroughly mixed and then aliquoted into bottles. To each bottle was added a different biocide. Three bottles were left unaltered; one was stored at −10 °C, one at 25 °C, and one at 25 °C in the dark. Over the course of seven months, samples were withdrawn from all bottles and analyzed for Ca, Mg, K, SO_4, NO_3, NH_4, Cl and PO_4 concentrations using standard analytical techniques (Galloway and Likens, 1976). Due to the inherent preserving nature of precipitation samples with low pH (<4.5) (Galloway and Likens, 1976), the pH of the aliquots was raised to 6.0 with NaOH. Even with this manipulation, little biological growth was expected because the precipitation used for this study was collected in mid-December and presumably was relatively free of biota. (In some

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[1] In this investigation an event is defined as any 24-hour period in which precipitation occurred.

Table 3. *Effect of sampling time on precipitation chemistry**

Sampling period	Volume	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
31 Dec. 74–17 Jan. 75	1.80	1.40	1.12	0.98	0.96	1.13	1.55	1.24	0.90	1.34	1.25
18 Jan.–7 Feb. 75	0.99	0.80	1.04	0.81	1.20	1.00	1.10	1.00	1.20	1.10	0.76
8 Feb.–27 Feb. 75	0.99	1.00	1.04	1.02	2.84	0.87	1.12	0.86	1.31	1.58	1.18
28 Feb.–21 March 75	1.10	0.98	0.90	0.88	0.91	1.13	0.90	0.83	0.80	1.07	0.69
22 March–8 April 75	1.20	1.58	0.94	0.92	1.55	0.96	1.09	1.05	1.02	1.64	0.95
10 June–10 July 75	—	1.06	0.51	0.71	0.83	0.65	1.21	0.80	3.06	1.43	0.84
10 July–5 Aug. 75	—	1.43	0.45	0.57	—	0.27	1.57	1.28	0.21	1.66	0.89
Mean ± SD	1.22 ± 0.34	1.18 ± 0.29	0.86 ± 0.27	0.84 ± 0.16	1.38 ± 0.76	0.86 ± 0.31	1.22 ± 0.25	1.01 ± 0.19	1.21 ± 0.89	1.40 ± 0.25	0.94 ± 0.21

* The table values represent the following ratio (R):

$$R = \frac{\text{sum of element amount in individually collected storms over a set period}}{\text{amount of element in a composite sample collected throughout same period}};$$

At $R = 1$, the extended sampling period had no adverse effect on the chemical loading;
At $R > 1$, the extended sampling period resulted in a lower estimate of chemical loading than did the sampling by event for that period;
At $R < 1$, the extended sampling period resulted in a larger estimate of chemical loading than did the sampling by event for that period.

Table 4. *Error variance* $(V_e)^*$ *in precipitation composition*

	A. Due to sampling time and collector separation	B. Due to collector separation only
Volume	0.083	0.027
H	0.0070	0.0018
SO_4	15.11	1.28
NO_3	6.23	0.09
PO_4	0.020	0.006
Cl	1.04	0.52
NH_4	5.81	0.01
Na	10.81	0.02
K	0.031	0.008
Ca	1.01	0.07
Mg	0.007	0.001

$$^*V_e = \frac{1}{n-1} \sum_{i=1}^{n} (e_i - \bar{e})^2,$$

where e = the difference between the element amount in:
A. two adjacent collectors, one a composite collector and the other a summed event collector and
B. two adjacent collectors sampled on an event basis.

precipitation samples with pH <4.5, collected in the summer and stored at room temperature without biocides, biological growth was observed after a period of nine months.)

The following is a listing by biocide of the problems experienced with the additive biocides. The concentration of the biocide in the sample is noted parenthetically. If the biocide had no effect on an element, then the element is not mentioned.

$CuSO_4$ (2 g/l)

This is a common biocide and is frequently used in freshwater systems to control the growth of algae. Its usefulness with precipitation samples is marginal. In addition to contaminating the sample with copper and sulfate, it also reacts with the Ca to form insoluble $CaSO_4$. The reagent grade that we used heavily contaminated the sample with PO_4 and NH_4, presumably from $Ca_3(PO_4)_2$ and $(NH_4)_2SO_4$ impurities in the reagent.

Na_2SO_3 (2 g/l)

Although this reagent has been used in the past it is generally unsuitable because sulfite is oxidized to sulfate, which in this case is not a biocide. Also, Ca and SO_4 are precipitated from the sample.

$Na_2S_2O_5$ (2 g/l)

The use of sodium metabisulfite precludes the analysis of sulfur and sodium because it overwhelms the ambient concentration in solution. It is also oxidized to SO_4 which will precipitate Ca. Due to impurities in the reagent grade that was used, or incompatibility with the analytical method, Cl analyses were spurious.

$HCHO$ (2 ml/l)

Formaldehyde rendered the sample unsuitable for the analysis of NO_3 and SO_4. In addition, over the course of the seven-month experimental period the concentration of soluble reactive phosphorus increased from 0.005 mg/l to 0.035 mg/l and NH_4 decreased from 0.095 mg/l to 0.040 mg/l. These changes are indicative of biological activity in the samples.

CH_3OH (2 ml/l)

Methanol either contaminated the sample with NO_3 or interfered with the analytical technique. It also produced a large variability in the K levels.

$CHCl_3$ (2 ml/l)

Chloroform had the same effect on K as did CH_3OH.

$C_6H_5CH_3$ (2 ml/l)

A large variability in the K analyses was observed when toluene was added. This variability (and that shown with the use of CH_3OH and $CHCl_3$) may be due to the presence of an organic phase in the samples.

$Hg(Ac)_2$ (2 g/l)

Mercuric acetate either contaminated the sample with PO_4, SO_4, NO_3 and Cl or it altered the analytical method to such a degree as to give spurious results. In addition, the acute sensitivity of the human organism to Hg is a major disadvantage to the use of this biocide.

The preserving techniques discussed above are all additive. In every case an adverse effect on the sample integrity was experienced. Based on these results it is not possible to recommend a biocide for use in the field: they all have disadvantages. However, it can be noted that of the biocides tested, chloroform and toluene had the least adverse effect on the sample composition.

The sample stored in the dark and the sample stored in the light at 25 °C showed no change in composition over the seven-month period. The sample stored at −10 °C showed a decrease in NH_4 concentration from 0.12 mg/l to 0.02 mg/l. It is somewhat ironic that the only samples exhibiting no significant change in composition were those samples that were unaltered. This situation provides an excellent example of the danger inherent in sample preservation.

8. Data reliability

Variability in data on precipitation chemistry has three sources—analytical, sampling and spatial.

Analytical variability is a precision barrier which limits the type of investigations on precipitation composition that may be attempted. Estimates of analytical variability in this study were obtained by analyzing ten aliquots of the same sample (Table 5). This would vary from laboratory to laboratory.

Sampling variability is defined as the difference in precipitation composition between samples collected at the same time, in adjacent collectors. This variability necessarily includes analytical variability. The magnitude of sampling variability was estimated in the following manner. Six bulk collectors were placed in the same area (149 m^2). For 15 precipitation events (each event included precipitation and the dry deposition that fell between the previous event and the sampled event) all collectors were sampled identically. The variability in the compositional data was tabulated to determine sampling variability (Table 5). The variability due to sampling is appreciable and is of greater magnitude than the analytical variability.

The third type of variability, spatial, is actually an extension of the second type. However, instead of the collectors being adjacent they are separated by a greater distance (1–1000 km). To determine the magnitude of spatial variability, three bulk precipitation collectors were placed in a rural area, 5 km in diameter. The collectors were sampled on an event basis (in addition to the rainfall from the single storm, each event included the dry deposition that fell between the previous storm and the sampled event) for 12 events and the coefficient of variation of the depositional and compositional fields determined for each event. Depositional and compositional fields are defined as the areal distribution of precipitation amount (cm) and composition (mg/l), respectively. Then a mean coefficient of variation was calculated (Table 5). In

Table 5. *The magnitude of sources of variability in precipitation composition**

	Analytical variability	Sampling variability	Spatial variability (Granat, 1976)	Spatial variability (this study)
Volume	0.01	0.05	0.33	0.06
H	0.06	0.11	—	0.09
SO_4	0.05	0.06	0.29	0.09
NO_3	0.01	0.06	0.32	0.09
NH_4	0.02	0.15	0.87	0.13
PO_4	0.12	0.31	—	0.72
Cl	0.04	0.29	—	0.54
Ca	0.00	0.12	—	0.14
Mg	0.03	0.22	—	0.16
Na	0.03	0.25	0.61	0.93
K	0.13	0.35	—	0.31

* The values are computed by dividing the standard deviation by the mean of the analyses. For analytical variability 10 aliquots of the same sample were analyzed and $\bar{x}$ and SD were computed. For sampling variability, 6 bulk collectors were sampled after 13 separate events, the composition determined and $\bar{x}$ and SD calculated for each parameter per event. For the first spatial variability, ~50 collectors spread over an area of 7600 km^2 were sampled on an event basis (7 events), SD/$\bar{x}$ was determined for each parameter per event and then summed and averaged for the 7 events (after Granat, 1976). For the second spatial variability (this study), 3 collectors were placed in an area 5 km in diameter, sampled on an event basis (12 events) and SD/$\bar{x}$ was determined for each parameter per event and then summed and averaged over the 12 events.

another investigation, Granat (1976) computed the spatial variability for an area 100 km in diameter. Fifty precipitation collectors were randomly positioned within the area and sampled on an event basis for seven events (Table 5).

In our study, the spatial and sampling variability for the chemical parameters were essentially equal, with the exception of Na, Cl and PO_4. This information indicates that to determine the precipitation composition for that area (excluding PO_4, Na and Cl), only one station is necessary. In the Granat (1976) investigation, the spatial variability is much greater than our sampling variability primarily because the size of the area (7600 km^2) is so large. If only one station were to be used to determine the chemical composition of the precipitation in that area, then the variability of those data (hence, the limits on interpretation) is determined by the spatial variability.

These two investigations provide an estimate of the variability of the data on precipitation composition that can be expected. From these studies it seems doubtful that the reliability of composition data on a spatial scale (~50 km in diameter) would be better than 20–60%, depending on the element. This is consistent with a previous investigation of variability (Karol and Myatch, 1972). This sets a definite limit on data use and interpretation. These factors should be taken into account when designing precipitation chemistry studies.

9. Proposed procedure for precipitation collection

Samples of precipitation are probably the most difficult water samples in nature to collect for chemical analysis. Not only is precipitation a dilute system (thus prone to contamination) but precipitation events are also a random occurrence. In sampling lakes, streams and oceans it is necessary to travel to the sampling site and exercise care about sampling techniques. For precipitation, in addition to the travel and careful sampling, it is also necessary to wait for precipitation to occur. This added difficulty emphasizes the care that must be taken in designing sampling procedures, constructing collectors and stabilizing samples. This report and several others (Granat, 1974a, 1976; WMO, 1974; Berry et al., 1975; Galloway and Likens, 1976) have addressed the problems of sampling precipitation for chemical analysis.

We have attempted to synthesize information on sampling precipitation for chemical analysis from these published reports. Because of the variety of potential research interests and the range of environmental conditions associated with precipitation, it was necessary to state objectives for the proposed procedure. A primary objective was to define an appropriate procedure for collection of representative samples of incident precipitation. A secondary objective was to insure that the sample was representative of the regional (area >50 km in diameter) composition of precipitation.

The siting of a precipitation collector is the fundamental problem in any precipitation collection project. The following criteria for site selection is a compilation from several sources (Granat, 1974a, 1974b, 1976; WMO, 1974) and the experience of the authors.

1. Select a general area free from the influence of local potential sources of atmospheric debris such as cities, roads, marshes, cultivated fields, smoke stacks, etc. If there are local sources, check wind direction data during precipitation events.

2. Select a specific location that is on a flat or gently sloping terrain and sheltered from the wind. A clearing in the forest with a grass cover is ideal. The surrounding forest acts as a natural wind shield, reducing the effects of wind on precipitation collection efficiencies. The potential site should be in an area that will be free of urban or industrial development for the duration of the project.

3. After the initial selection of a site, a large number of identical collectors should be placed on a grid pattern around the permanent collector at the site. The size of the grid (hence the number of additional collectors) is a function of the region to be represented by the permanent collector. Once the grid is established, the precipitation collectors should be sampled with the same frequency that will be used for the permanent collection in the planned research investigation. The grid will provide information on the availability of the depositional and compositional fields of precipitation. From this information a decision can be reached about the representativeness of the precipitation to be collected. Although the exact answer to the question of which component to collect depends on the research hypothesis of the investigator, there are a few basic principles that can be stated. If the research is designed to investigate the atmospheric inputs into an ecosystem, then bulk precipitation may be adequate

and perhaps even mandatory, if there is a substantial transport of large particles across ecosystem boundaries. If the data are to be used to investigate the chemistry of rain and snow, then dry fallout must be excluded from the samples. If precipitation samples are being collected for monitoring purposes, then the selection of precipitation components depends on the chemical parameters being monitored.

The intermittent nature of precipitation necessitates a collector that will function unattended in the field. The following criteria should be used to judge the reliability of a precipitation collector.

1. The collector must collect precipitation that is free of contamination and representative of the precipitation falling in the area of collection.

2. If automated, the moving and electrical parts must be dependable under a wide range of temperatures (−50 °C to 50 °C) and a variety of field conditions.

3. The collector must be simple, relatively inexpensive and easy to maintain and repair. The most sophisticated precipitation collector is not adequate if it does not function reliably in the collection of representative precipitation samples.

Because a precipitation collector is a less efficient collector than a standard rain gauge, it is advisable to install a recording rain gauge with a wind shield at the collection site. The precipitation amount information from the rain gauge, in conjunction with the composition information (corrected for evaporation) from the precipitation collector, should be used to calculate elemental deposition.

For the determination of the inorganic composition of precipitation, collection vessels should be plastic. The disadvantages of glass as opposed to plastic are the following:

1. Glass surface can act as an ion exchanger and alter the composition of the precipitation sample (Galloway and Likens, 1976).

2. Glass is prone to breakage. In freezing conditions, the glass may shatter due to expansion of the sample.

In our experience, sampling containers should be acid washed after each sampling event. This insures against random and systematic contamination from accumulated debris in the container. Briefly our procedure is the following: After pouring the sample from the sampling container, the container is checked for biological growth, soil particles and plant debris. If the container is visibly contaminated it is discarded, if not it is filled with 6 N HCl and allowed to sit for 1 hour after which it is thoroughly rinsed with deionized water. The conductivity of the final rinse is checked to insure that all the acid was removed. The container is then sealed until used. If the sample contains obvious foreign matter it should be discarded.

There are several factors that determine the length of the sampling period. Stability of the sample is the most important. If the measurement of a reactive parameter in precipitation is required (e.g. organic acids) then event sampling of precipitation is mandatory. However, if the required measurement is of a conservative parameter (e.g. volume) or if the sample is resistant to chemical change (e.g. most rural precipitation samples with pH <4.5 are essentially self-preserving), then the sampling schedule may be on a weekly, or in the extreme, on a monthly basis. However, even with a stable solution there is a finite limit that samples can remain in the field. This limit is variable and is dependent on random contamination, meteorological conditions, season, etc. We recommend a sampling period by event or by week, depending on the particular research objective. When the sampling period is greater than one week, the potential for sample contamination or alteration is greatly increased. In areas of the rural northeastern United States (New England, New York State), no biocide is necessary due to the low pH of precipitation (<4.5). Although this may not be the case in other areas, we would recommend a decrease in the length of the sampling period rather than use of a biocide.

Due to the dilute nature of precipitation samples, sensitive analytical techniques must be used to measure accurately the major ionic components. A listing of required sensitivity levels and analytical procedure used in this laboratory is presented in Table 6. Although this listing is not meant to be exclusive it represents a solid analytical foundation for the determination of the inorganic composition of precipitation.

There are several methods to test the quality of the analytical data. Two primary ones are the ratio, $\sum$ anion equivalents/$\sum$ cation equivalents, and the comparison of the measured conductivity to the calculated conductivity. If the ratio of the total anions (microequivalents/liter) to the total cations is not within 10% of unity then the analytical data should be checked and samples reanalyzed.

Table 6. *Analytical sensitivity levels necessary for the analysis of precipitation from a rural region*

Element	Sensitivity	Method
SO_4	0.1 mg/l	Lazrus et al. (1968)
NO_3	0.02 mg/l	Kamphake et al. (1967)
NH_4	0.02 mg/l	Solorzano (1969)
PO_4	0.002 mg/l	Murphy and Riley (1962)
Cl	0.05 mg/l	O'Brien (1962)
Na	0.005 mg/l	Atomic Absorption Spectrophotometer
K	0.01 mg/l	Atomic Absorption Spectrophotometer
Ca	0.01 mg/l	Atomic Absorption Spectrophotometer
Mg	0.005 mg/l	Atomic Absorption Spectrophotometer

The predictive conductivity is another standard method for quality control (Standard Methods, 1971). The specific conductivity for each ion is multiplied by its concentration and the products are summed to generate the predictive conductivity. This is compared to the measured conductivity. Again, if there is greater than a 10% deviation between the two, analyses should be rechecked.

10. Conclusion

This paper is one of a series of publications on the collection and chemical analysis of precipitation. While the first paper presented the results from an intercalibration of ten different designs of precipitation collectors (Galloway and Likens, 1976), this paper presents results of experiments on the collection efficiency of collectors, preservation of samples, monthly variation of wet and dry deposition, sample storage, length of sampling period, choice of collector location and sources of variability in precipitation data. The primary conclusions are that dry fallout should usually be excluded from rain and snow samples, sampling should be on an event basis, all biocides tested had some detrimental effect on sample composition, and that the major sources of variability in precipitation data are due to sampling errors and choice of collector location.

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СБОР ОСАДКОВ ДЛЯ ХИМИЧЕСКОГО АНАЛИЗА

Эта статья одна из серии публикаций по сбору и химическому анализу осадков. Тогда как в первой статье представлены результаты интеркалибрации 10 коллекторов различной конструкции (Галловэй и Ликенс, 1976), здесь описаны результаты экспериментов по эффективности сбора коллекторов, сохранению проб, месячным вариациях жидкой и сухой фракций, длине периода сбора, выбору места коллекторов и источникам изменчивости и данных по осадкам. Основными выводами являются, что сухая фракция осадков должна обычно исключаться из проб дождя и снега, отбор должен быть связан с фактами выпадения осадков, все проверявшиеся биоциды имеют некоторые нежелательные эффекты на состав проб, и что главными источниками изменчивости в данных по осадкам являются ошибки выборки и выбор места коллектора.