CALIBRATION OF COLLECTION PROCEDURES FOR THE DETERMINATION OF PRECIPITATION CHEMISTRY[1]

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ABSTRACT

Precipitation is currently collected by several methods, including several different designs of collection apparatus. We are investigating these differing methods and designs to determine which gives the most representative sample of precipitation for the analysis of some 25 chemical parameters. The experimental site, located in Ithaca, New York, has 22 collectors of 10 different designs. The designs include bulk (wet and dry deposition collected together), wet only (only rain and snow) and wet/dry (collects wet and dry deposition separately). In every sampling period, which varies from one day to one month, depending on the time variable being tested, the following chemical parameters are determined: conductivity, pH, Ca, Mg, Na, K, NH_4, NO_3, N_{total}, SiO_4, PO_4, P_{total}, Cl, SO_4, DOC, Zn, Cu, Mn, Fe, Al, Ni, Cd, Pb, Ag, DDT, DDE, Dieldrin and PCB's.

The results of the investigation lead us to conclude that:

1. Precipitation samples must exclude dry deposition if accurate information on the chemical content of precipitation is required.
2. Substantial contamination results when glass and plastic collectors are used to sample precipitation for inorganic and organic components, respectively.
3. The inorganic components of precipitation samples of low pH (3.5-4.5), with the exception of PO_4 and Cl, exhibited no significant change in concentration when stored at 4 C for a period of eight months. We believe this is due to the stabilizing influence of a large concentration of hydrogen ions.
4. If quantitative information on the chemical composition is required, precipitation samples should be collected at no longer than weekly intervals if immediate collection is not possible.

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I. INTRODUCTION

The current studies of precipitation chemistry underway in the United States include precipitation networks operated by the U.S. Geological Survey and the Environmental Protection Agency. Unfortunately, a wide variety of collection procedures, sampling devices and analytical procedures are utilized in these studies. This problem of diversity of techiques also applies to historical investigations of precipitation chemistry (MacIntire and Young 1923, Wilson 1926, Collison and Mensching 1932, Leland 1952, Carroll 1962, Gambell and Fisher 1966, Lodge et al. 1968, Pearson and Fisher 1971, Likens 1972, Likens and Bormann 1974). Because of the importance of establishing reliable benchmark data and evaluating trends in the composition of precipitation, some calibration of current data-collection procedures is urgently needed. This paper describes an investigation of the calibration of collection procedures for the determination of precipitation chemistry.

The major problems in attempting to characterize the chemical composition of precipitation are related to the collection and storage of samples, rather than analytical difficulties. These problems include (1) the effect of the design of the collector in obtaining a representative sample of precipitation and its chemical content; (2) geochemical or biological changes occurring within the container once the sample has been collected, as related to the presence of foreign particles in the samples or on a filtering apparatus through which the precipitation passes; (3) effect of storage, including *in situ* collection time, on chemical composition; (4) leaching or absorption of substances from or to collector surfaces; and (5) effects of sampling interval, both during intra- and inter-storm periods.

II. PROCEDURES

A. COLLECTOR LOCATION

Twenty-two precipitation collectors (ten different designs) were used in the calibration investigations. A listing of the collectors is presented in Table I. The collectors were positioned randomly in an enclosure near the Department of Commerce (NOAA) Climatological Data Network Station at the Cornell University Game Farm in Ithaca, New York. Climatological data from the weather station was used to determine the amount of precipitation and the wind direction at the intercalibration site. In addition, a long history of precipitation chemistry for the area, dating to 1918, was available.

The intercalibration site became operational on 1 August 1974. This report covers the period from 1 August 1974 to 1 May 1975.

TABLE I

Collector	N	Type	Manufacturer	Container Material
Hubbard Brook Rain (HB)	6	Bulk*	Hubbard Brook Project	plastic
Hubbard Brook Snow (SN)	3	Bulk	Hubbard Brook Project	plastic
Bulk Glass (BG)	3	Bulk	this laboratory	glass
Misco (MS)	3	Wet**	Misco Scientific	plastic
Wong (WOG)	2	Wet	Wong Scientific	plastic
Swiss (ERN)	1	Wet	ERNI and Company	stainless steel
Finnish (FIN)	1	Wet/Dry†	Parelco Oy, Finland	plastic
USAEC (AEC)	1	Wet/Dry	U.S. Atomic Energy Commission	plastic
ISWS (GEM)	1	Wet/Dry	Illinois State Water Survey	plastic
Swedish (ING)	1	Wet/Dry	Lennart Granat, Sweden	glass

* A BULK collector is open to the atmosphere at all times and collects both wet and dry deposition.

** A WET collector is a powered collector open to the atmosphere only when it rains or snows.

† A WET/DRY collector is a powered collector that samples precipitation and dry deposition in separate containers.

Each precipitation sample was analyzed for Ca, Mg, K, Na, NH_4, H, SO_4, NO_3, Cl, PO_4, SiO_4, conductivity and DOC, while in selected samples PCB, DDT, DDE, Dieldrin, Aldrin, Zn, Cu, Cd, Ni, Ag, Fe, Mn and Al were determined. In this report only the first group of chemical compounds will be discussed.

B. ANALYTICAL

The analyses for Ca, Mg, K and Na were performed on a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Appropriate amounts of lanthanum and HCl were added to subsamples to avoid interferences with the Ca and Mg determinations. Hydrogen ion concentration was determined with a pH meter. Standard procedures adapted and automated for use with a Technicon Autoanalyzer were used for analysis of NH_4, NO_3, SO_4, PO_4, Cl, and SiO_4. NH_4 was determined by an alkaline phenolhypochlorite method (Solorzano 1969), NO_3 by hydrazine reduction (Kamphake et al. 1967), SO_4 by colormetric measurement of barium-thymol blue complex (Lazrus et al. 1968), Cl by the liberation of thiocyanate ion from mercuric thiocyanate in the presence of ferric iron (O'Brien 1962) and dissolved SiO_4 by reduction of silicomolybdate to heteropoly blue with aminonaphtholsulfonic acid (American Public Health Association 1965). Soluble reactive phosphate was determined from a molybdenum blue complex after reduction with ascorbic acid in the presence of a small amount of antimony (Murphy and Riley 1962).

All collection containers were acid washed after each sampling. The plastic containers were washed with 6N HCl and rinsed with deionized water. The glass containers were washed with chromic acid and rinsed with double distilled water. Samples were stored at 4 C until time of analysis.

III. RESULTS AND DISCUSSION

A. COLLECTOR RELIABILITY

The effect of collector design on the collection efficiency of precipitation is presented below together with the mechanical and structural problems associated with each collector type.

1. Bulk Collectors

Hubbard Brook Rain Collector (HB) - Bulk

This collector is composed of a plastic funnel attached to a plastic bottle by a length of plastic tubing. An additional bottle, which acts as a vapor trap, and a loop in the plastic tubing prevent evaporative losses from occurring. The only source of difficulty experienced with this design was that the clamps holding the components to the supporting stand had a tendency to become loose, thus affecting the collection efficiency when the funnel tilted.

Hubbard Brook Snow Collector (SN) - Bulk

This collector is a large plastic garbage can that is secured to a wooden post such that the collector opening is five feet from the ground. This is an excellent collector for snow samples as it collects large amounts of precipitation due to the large opening of the collector.

Glass Collector (BG) - Bulk

Aside from the contamination problem resulting from the glass (Section III-B), there are no obvious design problems except that the sample in this open collector is subject to evaporation. However, the glass contamination makes this collector unsuitable for most all chemical parameters except pesticides, PCB's and other organics and a few inorganic species.

2. Automated Collectors

The potential problems associated with automated collectors are much greater than those associated with bulk collectors. For proper sampling the collector motor, sensor and thermostat must all be operating perfectly. It is clear that if a collector is not mechanically reliable for extended periods in the field, then it is of little use in the collection of precipitation. The following description of the automated collectors tested in this investigation relies heavily on mechanical integrity.

Misco Collector (MS) - Wet

The Misco collectors have a sliding lid that uncovers the collection vessel during precipitation. Of the three Misco collectors, only one operated satisfactorily, while the other two worked about fifty percent of the time in both rain and snow collection (Tables IIA and IIB). The primary problem with this collector was that the motors failed. Counting the three original motors, a total of six motors have been used to keep these collectors operating. For the field operator, this is a very expensive situation, in both money and time.

TABLE IIA

RELIABILITY OF AUTOMATIC COLLECTOR IN SUMMER AND FALL 1974*

Collector	MS1	MS2	MS3	FIN	AEC	GEM	ERN	WOG	ING
1 Aug- 8 Aug	o	o	-	o	o	-	x	-	-
9 Aug-15 Aug	o	o	-	o	o	-	x	-	-
16 Aug-22 Aug	o	o	-	o	o	-	x	-	-
23 Aug-29 Aug	o	x	-	o	o	-	x	-	-
30 Aug- 5 Sep	o	x	-	x	o	-	x	-	-
6 Sep-12 Sep	o	x	-	x	o	-	x	-	x
13 Sep-19 Sep	o	x	-	x	o	-	x	-	x
20 Sep-26 Sep	o	x	-	x	o	-	x	-	x
27 Sep- 3 Oct	o	x	o	x	o	-	o	-	x
4 Oct-10 Oct	o	o	x	o	o	-	x	-	x
11 Oct-17 Oct	o	o	x	o	o	-	x	-	x
18 Oct-24 Oct	o	o	x	o	o	o	x	o	x
25 Oct-31 Oct	o	x	o	o	o	o	x	x	x
1 Nov- 7 Nov	o	x	o	o	o	o	x	x	x
8 Nov-14 Nov	o	x	o	o	o	o	x	o	o

* o = collector functioning at beginning of week

x = collector not functioning at beginning of week

\- = collector not available

In addition, on the rare occasion when all three collectors were operating simultaneously and when all three sensing adjustments were set at their most sensitive position, the three collectors collected different amounts of precipitation. In winter substantial amounts of time were spent on maintaining the thermostats and heating elements in the sensing units. Undoubtedly, part of the variation in collection efficiency (Table IV) between the different Misco collectors was a result of thermostat malfunction

This collector has a very bad splash problem, i.e., the collection vessel sits below the metal rim of the collector and the sliding cover is adjacent and above the collection vessel. In addition, the area of the opening is too small (0.0143 m^2) to collect ample precipitation for complete chemical analysis unless the storm is large (>2 cm of rain).

TABLE IIB

RELIABILITY OF AUTOMATIC COLLECTOR IN WINTER AND SPRING 1974-1975*

Collector	MS1	MS2	MS3	FIN	AEC	GEM	ERN	WOG	ING
6 Dec-12 Dec	o	x	o	o	o	o	x	x	o
13 Dec-19 Dec	o	x	o	o	o	o	x	x	o
20 Dec-26 Dec	o	x	o	o	o	x	x	x	o
27 Dec- 2 Jan	o	x	o	o	o	x	x	x	o
3 Jan- 9 Jan	o	x	x	o	o	x	x	x	o
10 Jan-16 Jan	o	x	x	o	o	x	x	x	o
17 Jan-23 Jan	o	o	o	x	o	x	x	x	o
24 Jan-30 Jan	o	o	o	x	o	x	x	x	o
31 Jan- 6 Feb	o	x	o	x	o	x	x	x	o
7 Feb-13 Feb	o	x	o	o	x	o	x	o	x
14 Feb-20 Feb	o	x	o	o	x	o	x	o	x
21 Feb-27 Feb	o	x	o	o	x	o	x	o	x
28 Feb- 6 Mar	o	o	x	x	x	o	x	x	x
7 Mar-13 Mar	o	o	x	x	x	o	x	x	x
14 Mar-20 Mar	o	o	x	x	x	o	x	x	x
21 Mar-27 Mar	o	o	x	x	x	o	x	x	x
28 Mar- 3 Apr	o	o	x	x	x	o	x	x	x
4 Apr-10 Apr	o	o	x	x	x	o	x	x	x
11 Apr-17 Apr	o	o	x	x	o	x	x	x	x
18 Apr-24 Apr	o	o	x	x	o	x	x	x	x
25 Apr- 1 May	o	o	x	o	o	x	x	o	x

* o = collector functioning at beginning of week

x = collector not functioning at beginning of week

TABLE III

THE EFFECT OF A GLASS COLLECTOR ON PRECIPITATION CHEMISTRY *

Sample period	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
9 Aug-17 Aug 74	0.85	0.48	0.49	3.0	2.3	1.3	1.2	1.5	1.3	0.98
18 Aug-24 Aug 74	0.76	1.2	1.2	1.8	2.4	1.1	1.0	1.5	-	0.93
4 Aug-28 Oct 74	-	1.2	1.5	4.6	3.0	-	2.0	-	-	-
29 Aug- 5 Nov 74	-	0.74	0.90	2.2	1.1	-	1.0	1.4	-	-
5 Nov-13 Nov 74	-	1.3	1.0	2.0	1.9	-	1.1	1.2	-	-
29 Oct-13 Nov 74	0.79	0.69	0.73	1.0	1.0	-	-	-	-	-
13 Nov-25 Nov 74	1.0	0.60	0.69	1.5	2.3	-	-	-	1.6	1.0
Mean ± Std. Error	0.85±.05	0.88±.13	0.93±.13	2.3±.4	2.0±.3	-	1.3±.2	1.4±.1	-	0.97±.02

* The table values represent the following ratio:

$$R = \frac{\text{Mean of concentration in bulk glass collector (N=1)}}{\text{Mean of concentration in bulk plastic collector (N=6)}}$$

At R=1, glass and plastic collectors have no or identical effect on sample chmistry

At R>1, glass collector contaminated sample or plastic collector adsorbed element from sample

At R<1, plastic collector either contaminated sample or glass collector adsorbed element from sample

TABLE IV

MEAN COLLECTION EFFICIENCY (percent) AS
A FUNCTION OF COLLECTOR TYPE & PRECIPITATION TYPE

	Rain	Snow
HB	90	--
SN	--	74
MS1	88	69
MS2	85	52
FIN	81	85
AEC	84	86
ING	--	73
WOG	82	--
GEM	--	76

Wong Collector (WOG)

Mechanically this collector worked relatively well; it suffered from an initial handicap in that it was not a new instrument as were the other collectors that we tested. The major maintenance problem we had with the collector was with the sensing unit; it corroded very quickly and thus the sensitivity to precipitation varied with time.

This collector has a large amount of metal area that precipitation can splash off of into the collector. This is especially true in the winter when a sloping roof is placed on the sliding cover to prevent snow accumulation. In addition, there is a gap between the sliding lid and the collection vessel, allowing dry deposition to contaminate the rain or snow sample.

ERNI Collector

A wet only collector, the ERNI has the best designed covering system of any of the automatic collectors. When the collector is open, the lid is entirely removed from the sampling orifice. There is little possibility of splash occurring. However, since the original collector we received has not functioned consistently because of electronic problems, further comparisons with other designs are not possible.

Finnish Collector (FIN)

Despite the poor record of performance for the FIN collector (Tables IIA and IIB), this has been one of the most mechanically reliable collectors. The primary problem is that the manfacturer is in Finland, and therefore replacement parts may take a long time to arrive. This collector is rugged, well suited for field work and, as will be illustrated in the following section, collects reliable samples of precipitation for most chemical parameters.

U.S. Atomic Energy Commission Collector (AEC)

This collector has been the most reliable of all the automatic collectors. Both the design and the construction of the collector are well suited for collection of wet and dry deposition in the field. The construction is rugged, which is of importance in the winter when ice and snow can accumulate on the collector. The sample containers have large openings (.0683 m^2), enabling one to collect 0.175 ℓ of precipitation with 0.25 cm of rainfall. This is four times the volume that our smallest collector (Misco) would collect with an equivalent amount of precipitation. There exists the possibility of contamination from splash due to the large lid that covers the collection vessels.

Illinois State Water Survey Collector (GEM)

This collector is built from the blueprints of the AEC collector with the exception that it is poorly constructed, which results in severe and rapid deterioration of the gears in the drive unit. We have used three sets of gears in six months. This illustrates very well the importance of constructing a strong collector for use in the field.

Granat Collector, Sweden (ING)

This collector was lent to us by Dr. Lennart Granat, University of Stockholm, Sweden. This is the most intricate collector that we have, and is a finely tooled and machined instrument. Unfortunately, its tolerances for routine field collection of precipitation are too fine. It does not withstand abuse, and is awkward to transport. At its best it collects samples just as well as the other collectors, but it is subject to too many small aberrations that compromise the integrity of the precipitation sample. However, of all the wet/dry collectors, this one has the best design to prevent splash problems; the two collection vessels are far apart without any large expanse of metal between them. There may be some problem from the brass lid, but this has not been evaluated.

B. MATERIALS

The materials primarily used in the construction of the collection vessels are plastic (polyethylene) and glass (pyrex). The project has sixteen plastic collectors and five glass collectors. The comparison between samples collected in the bulk plastic (N = 6) and the bulk glass (N = 1) is given in Table III. The values are ratios of the mean of concentration for the bulk glass divided by the mean of the concentration for the bulk plastic. The ratios indicate the following:

ratio = 1, no, or similar, contamination or adsorption from either collector

ratio > 1, contamination from the glass collector or adsorption by the plastic collector

ratio < 1, contamination from the plastic collector or adsorption by the glass collector

It is obvious that the glass collector seriously contaminates a precipitation sample with respect to Na, K and PO_4. It also appears that a sample collected in glass may be contaminated with Cl, although there are only two sampling events. Glass has a much more active surface than plastic; therefore, ratios that are less than one may be explained by adsorption of the chemical species on the glass surface. This is certainly possible for hydrogen.

C. EFFICIENCY OF PRECIPITATION COLLECTION

The mean efficiency of collection of rain and snow is presented in Table IV. This is defined as the volume collected, multiplied by 100, divided by the volume expected as determined by the weather station. As is evident the bulk collectors and the Misco collectors have lower sampling efficiencies in the winter. For the Misco collectors the malfunctioning of the thermostat causes the poor efficiency. The lower collection efficiency of the Hubbard Brook snow collector (SN) is due to the effect of blown snow and wind turbulence. The FIN and AEC have about identical collection efficiencies for rain and snow.

D. PRECIPITATION CHEMISTRY REPLICABILITY AS A FUNCTION OF COLLECTOR TYPE

Operationally the collectors are divided into the following functional groups.

Bulk plastic:	collects bulk precipitation with plastic containers (HB, SN).
Wet plastic:	collects wet precipitation with plastic containers (AEC, MS, FIN and GEM).
Dry plastic:	collects dry precipitation with plastic containers (AEC, FIN and GEM).

The chemical replicability data for the above classes of collectors are presented in Table V. The values in the table represent the standard error, multiplied by 100 and divided by the mean for each chemical species per storm. Then all the storm events were summed and a "mean" percent error was determined. These values give an indication of the percent error in determining a chemical species when N samplers of the same design are used.

TABLE V

MEAN PERCENT ERROR$^+$ IN CHEMICAL ANALYSIS OF PRECIPITATION AS A FUNCTION OF COLLECTOR TYPE AND PRECIPITATION TYPE

Collector Type	N	Volume	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
Bulk Plastic* (rain)	6	3.2	5.2	4.8	7.0	7.1	12	4.4	2.6	25	19	3.8
Bulk Plastic** (snow)	3	1.9	4.7	2.8	3.0	4.7	6.8	1.5	2.1	17	13	2.4
Wet Plastic* (rain)	6	-	8.4	17	34	16	20	21	5.8	32	20	6.4
Wet Plastic** (snow)	6	-	8.6	25	28	28	12	12	10	20	28	11
Wet Plastic** (snow) (except Misco)	3	-	5.9	22	14	19	9.3	4.8	5.2	15	27	5.8

* average of 8 sampling events

** average of 7 sampling events

+ For each sampling event, an elemental mean and standard error was determined for all collectors of the same type (bulk or wet plastic). The standard error, divided by the mean and multiplied by 100 was defined as PERCENT ERROR. The MEAN PERCENT ERROR tabulated here is the mean of the PERCENT ERRORS for all sampling events.

For the bulk plastic collectors it is evident that except for PO_4, Cl and K the error is less than ten percent in both the rain and snow collectors. This implies that the bulk plastic samplers collect identical samples, and that the sample does not vary in chemical composition while in the collector. The percent error is generally lower in the bulk snow collectors, presumably because of the lower amount of biological activity in the winter.

The percent errors are larger in the wet plastic collectors than the bulk plastic. The wet plastic collectors are all of different designs and construction materials, unlike the bulk plastic which were of identical design and construction. In addition, the bulk plastic collectors were completely cleaned after every sampling event, while in the wet plastic collectors only the actual collection vessel was cleaned and the metal superstructure of the sampler was not. Thus a burden of dust and impacted aerosols could accumulate on the metal superstructure and possibly contaminate future samples by splash. In addition, it appears that the Misco collectors contribute significantly to the large error values. Comparing the wet plastic (snow) numbers, which represent all of the wet plastic collectors, with the wet plastic (snow, except Misco) numbers, which represent all the percent errors decrease in the latter instance, often by a factor of two. It appears that the most conservative chemical parameters are H, NO_3 and SO_4 in both the rain and snow samples.

E. EFFECT OF SAMPLING INTERVAL ON PRECIPITATION CHEMISTRY

At the beginning of the sampling period two bulk collectors (SN) were placed at the site; one was sampled and replaced after every storm and the other was sampled after three storms. The amounts of each element in the three samples from the first collector were totalled and compared to the composite sample of the three storms in the second collector. The results are presented in Table VI as ratios (total in individual storms/composite of sampling period).

TABLE VI

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	1.8	1.4	1.2	.98	.95	1.1	1.6	1.2	-	1.3	1.2
17 Jan- 7 Feb 75	.99	.80	1.0	.68	1.2	1.0	2.8	1.0	1.2	1.1	.76
7 Feb-27 Feb 75	.99	.86	.93	1.5	2.7	.98	1.0	.93	.82	1.5	.92
27 Feb-21 Mar 75	1.1	.94	.87	.85	.87	1.0	.93	1.1	.64	1.0	.70
21 Mar- 4 Apr 75	1.2	1.4	.95	.90	1.4	.98	1.1	1.1	1.0	1.3	.98

*The table values represent the following ratio:

$$R=\frac{\text{Sum of element amount in individually collected storms over a set period.}}{\text{Amount of element in a composite sample collected over same period.}}$$

At R=1, a three week sampling period had no adverse effect on the chemical composition.

At R>1, the three week sampling period resulted in a lower estimate of chemical composition then did the sampling by event for that period.

At R<1, the three week sampling period resulted in a larger estimate of chemical composition then did the sampling by event for that period.

Considering that the composite samples were in the field for a period of two to four weeks, the agreement between the sum of the individual events and the composite samples is good. A large degree of the agreement is undoubtedly caused by the low pH of the precipitation and the fact that the experiment was performed in the winter, when biological activity is at a minimum.

F. COLLECTION OF DRY DEPOSITION, BULK VS. WET/DRY COLLECTORS

It is of importance to know if the composition of a precipitation sample collected in a bulk sampler is identical to the sum of the compositions collected in a wet sampler and a dry sampler. Table VII presents results of eight comparisons between wet/dry collectors and bulk collectors that sampled the same event. These data are presented as ratios, amount of element deposited per unit area by wet precipitation plus amount of element deposited per unit area by dry deposition, divided by the amount of element deposited per unit area by bulk precipitation. If the ratio equals one, it indicates that the bulk and the wet/dry collector sample dry deposition with equal efficiency. If the ratios are greater than one, it means that either the wet/dry collector is contaminating the sample or that the bulk collector is losing the sample. Conversely, if the ratio is less than one, the reverse is true; the bulk sampler is contaminating the sample or the wet/dry collector is losing the sample.

TABLE VII

A COMPARISON BETWEEN THE COMPOSITION OF PRECIPITATION AS DETERMINED BY A BULK COLLECTOR AND BY THE SUM OF A WET AND DRY COLLECTOR*

Event	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
15 Sep 74-27 Sep 74	0.98	1.03	1.22	1.16	0.87	1.00	--	0.66	1.49
27 Sep 74- 4 Oct 74	1.09	1.19	0.81	1.16	0.68	0.84	0.65	0.84	1.48
4 Oct 74-28 Oct 74	1.01	1.09	1.25	1.20	0.95	1.10	--	0.95	1.42
13 Nov 74-25 Nov 74	0.92	0.86	1.01	1.44	1.00	0.99	1.43	0.96	1.14
6 Dec 74-18 Dec 74	0.99	0.84	1.15	1.29	1.13	0.97	0.94	1.56	1.04
18 Dec 74-31 Dec 74	0.79	0.67	0.99	1.24	1.54	1.10	0.74	1.09	1.05
31 Dec 74-17 Jan 75	1.03	1.40	1.09	1.21	--	--	--	1.29	1.71
7 Feb 75-27 Feb 75	1.41	1.19	1.14	1.10	0.95	0.91	0.54	0.73	1.08
Mean ± Std. Error	1.02±.06	1.04±.03	1.08±.05	1.22±.04	1.02±.10	0.99±.04	0.86±.16	1.01±.11	1.30±.09

*The table values represent the following ratio:

$$R = \frac{\text{AMOUNT IN WET COLLECTOR + AMOUNT IN DRY COLLECTOR}}{\text{AMOUNT IN BULK COLLECTOR}}$$

The comparisons are better than one would expect (Table VII). In fact, for NO3 and to a lesser extent Mg and Ca (and in the winter, SO_4), the results are very close, indicating that the dry/wet totals are certainly comparable to the bulk samples (Table VII).

G. INFLUENCE OF DRY DEPOSITION ON PRECIPITATION CHEMISTRY

The previous section has discussed the reliability and efficiency of collecting dry deposition; this section discusses the influence of dry deposition on the chemical composition of rain and snow.

Dry deposition is defined as the material that is added to ecosystems through the atmosphere when it is not raining or snowing. The term is somewhat nebulous with several components, such as direct particle fallout, aerosol impaction onto foliage and gaseous adsorption by the ground or foliage. Our collection devices measure particle deposition by gravity and almost no impaction or gaseous inputs. They, therefore, are underestimates of the material added to ecosystems during periods of no rain or snow.

We use two methods to assess the importance of dry deposition on the chemistry of rain and snow collected in a bulk precipitation collector. The first is to compare, for the same period, the composition of the bulk sample (wet and dry deposition) to the composition of the wet only sample; this is of course dependent on the amount of rain that fell and the length of time the bulk sampler collected dry deposition. This technique of comparison of bulk vs. wet collection arrives at a value for dry deposition by difference. The second method is to make the actual measurements of wet and dry deposition separately.

Measurement of the Influence of Dry Deposition on Wet Precipitation by Difference

The ratio of the mean of the species concentration collected in a bulk sampler vs. the mean of the species concentration collected in a wet sampler is presented as a function of season (Table VIII). The August-November bulk samples were collected in the Hubbard Brook rain collectors. The December-March bulk samples were collected in the Hubbard Brook snow collector. The wet only collectors for both time periods were identical. The ratios indicate the following:

ratio > 1, species in question is a component in both wet and dry deposition.

ratio = 1, species in question is a component in wet only precipitation.

ratio < 1, species in question is affected in some way by the mixture of wet and dry deposition.

The results of the August-November collection period indicate that there is a substantial dry deposition influence on the chemistry of the bulk precipitation samples for Ca, Mg and PO_4. For K, NH_4, NO_3, SO_4 and perhaps Cl, there appears to be a negligible contribution from dry

TABLE VIII

A COMPARISON OF THE CHEMICAL COMPOSITION OF BULK VERSUS WET PRECIPITATION*

Event	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
9 Aug 74-17 Aug 74	1.06	2.6	2.3	.62	.93	.53	.80	1.2	1.0	1.1
17 Aug 74-24 Aug 74	.95	.93	.95	.82	.82	.98	.98	1.3	-	1.1
1 Sep 74-13 Sep 74	.83	-	2.2	.74	1.2	.79	1.0	1.4	-	1.0
15 Sep 74-27 Sep 74	.88	2.0	1.7	1.1	1.5	1.2	.98	3.7	-	.86
27 Sep 74- 4 Oct 74	1.00	1.6	1.5	1.1	.93	1.4	1.1	2.0	.87	.95
4 Oct 74-28 Oct 74	.77	2.3	1.4	1.5	1.5	1.4	1.1	.80	1.4	.93
29 Oct 74-13 Nov 74	-	1.8	1.6	.9	.71	1.0	1.0	1.5	1.1	.92
13 Nov 74-25 Nov 74	.91	2.8	.90	2.7	1.4	1.4	1.3	1.3	2.6	1.1
6 Dec 74-18 Dec 74	.93	1.6	.88	1.7	1.0	1.4	1.2	1.1	1.5	1.1
Mean ± Std. Error	.92±.03	2.0±.2	1.5±.2	1.2±.2	1.1±.1	1.1±.1	1.1±.1	1.6±.3	1.4±.3	1.0±.0
18 Dec 74-31 Dec 74	1.3	7.6	2.8	5.3	2.6	3.9	2.3	2.6	2.5	2.3
31 Dec 74-17 Jan 75	1.2	4.4	4.8	5.7	2.8	2.3	2.3	2.5	3.6	1.5
17 Jan 75- 7 Feb 75	.66	4.7	3.5	4.7	2.9	1.7	2.1	1.6	2.8	1.8
7 Feb 75-27 Feb 75	1.3	2.8	1.8	2.3	1.4	1.8	1.5	2.2	2.0	1.4
27 Feb 75-21 Mar 75	.94	2.9	2.4	2.1	1.7	1.7	1.7	1.0	1.6	1.3
21 Mar 75- 4 Apr 75	1.1	-	4.1	4.7	2.0	1.9	1.8	1.4	4.9	1.6
Mean ± Std. Error	1.1±.1	4.5±.9	3.1±.5	4.1±.6	2.2±.3	2.2±.3	2.0±.1	1.9±.3	2.9±.5	1.6±.1

*The table values represent the following ratio:

$$R = \frac{\text{MEAN OF CONCENTRATION IN BULK PLASTIC COLLECTOR}}{\text{MEAN OF CONCENTRATION IN WET PLASTIC COLLECTOR}}$$

deposition. It is especially interesting that the ratio for hydrogen is less than one. This indicates that some of the acidity in the rain is being neutralized by the dry deposition component. In the December-March samples it is evident that all species, with the exception of H, have a large dry deposition component, which for some elements (Ca, Mg, and Na) completely dominates the chemistry of bulk precipitation samples.

Therefore, the influence of dry deposition on the composition of samples is much larger in the winter and affects all parameters measured, while in the summer and autumn it is only the terrestrial components (Ca, Mg and PO_4) that are affected.

Measurement of the Influence of Dry Deposition on Wet Precipitation by Actual Analysis

The second method of determination of the dry deposition influence on bulk precipitation samples is to measure it actually with a separate collection vessel. A summary of the second method and a comparison to a summary of the first method is presented in Table IX. It is evident

TABLE IX

THE INFLUENCE OF DRY DEPOSITION ON PRECIPITATION SAMPLES

	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
					Rain Samples				
Bulk Rain/Wet	2.0± .2	1.5± .2	1.2±.2	1.1±.1	1.1± .1	1.1±.1	1.6±.3	1.4±.3	1.0±.1
Wet & Dry/Wet	3.2±1.7	3.5±1.8	2.4±.7	2.1±.5	1.7± .2	1.2±.1	1.5±.2	1.9±.7	1.4±.1
					Snow Samples				
Bulk Snow/Wet	4.5± .9	3.1± .5	4.1±.6	2.2±.3	2.2± .3	2.0±.1	1.9±.3	2.9±.5	1.6±.1
Wet & Dry/Wet	4.4±1.8	3.1± .4	4.0±.7	2.3±.5	3.0±1.6	1.6±.1	1.6±.1	1.6±.2	2.0±.6

that in December-March (snow samples) the agreement between the two methods is quite good; they both show that the dry deposition component contributes significantly to the composition of the bulk sample. For the August-November period (rain) the agreement is poor, especially for Ca, Mg and Na, which have large dry deposition components. The reason for the poor agreement in the August-November period as opposed to the good agreement in December-March is due to the design of the dry deposition collector. In the rain period, the bulk collector is a funnel/bottle apparatus arrangement and the individual dry deposition collector is an open-mouthed cylinder, two very different designs, while in the snow period, both the bulk and the wet/dry collectors are open-mouthed cylinders. It appears that the open-mouthed barrel collects dry deposition more efficiently than the shallow funnel, but it is not clear which of these collects the most representative sample of dry deposition. Two opposing arguments can be made for each type of collecttor. On one hand the funnel, because of its shallow nature, will lose dry deposition due to the scouring action of the wind. However, it also can be argued that the open-mouthed cylinders can act like a snow fence, and therefore collect more dry deposition than is representative. This problem will be investigated further in the second year of the project.

It is apparent that regardless of the type of bulk collector used, the collection of dry deposition with wet precipitation can severely affect the apparent chemical composition of the rain and snow, sometimes by factors of two to three. Therefore it is recommended that wet only collectors be used in any determination of precipitation chemistry.

H. EFFECTS OF STORAGE ON PRECIPITATION CHEMISTRY

The effect of storage on the chemical integrity of the precipitation sample has been studied in the following manner. Twelve liters of precipitation were well mixed and then divided into three equal fractions. The first fraction was put on a shelf in the laboratory at 21 C. The second aliquot was put in the refrigerator at 4 C. The third aliquot was subaliquoted into one hundred 30-cc bottles and frozen at -4 C. Aliquots of the three fractions have been analyzed for the different chemical species over the course of seven months (Table X).

TABLE X

EFFECTS OF STORAGE ON CHEMICAL COMPOSITION OF PRECIPITATION SAMPLES

	pH	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
A. Sample Stored at 21°C.										
Nov 1974	3.91	.40	.061	.063	.042	.37	2.15	.004	.43	4.2
Dec	-	.43	.061	-	-	.43	-	-	.91	3.9
Jan 1975	-	.38	.043	.065	.039	.42	2.20	.026	.92	4.0
Feb	4.03	-	-	-	-	-	-	-	-	-
Mar	-	.45	.061	.064	.043	.42	2.05	.030	.86	4.2
Apr	-	.42	.063	.064	.035	.38	-	-	1.28	3.9
B. Sample Stored at 4°C.										
Nov 1974	4.03	.42	.063	.065	.039	.38	2.20	.004	.44	4.5
Dec	-	.42	.064	-	-	.43	-	-	.94	4.0
Jan 1975	-	.38	.042	.065	.039	.43	2.20	.018	.97	3.8
Feb	4.06	-	-	-	-	-	-	-	-	-
Mar	-	.44	.061	.064	.040	.38	2.15	.019	.92	4.0
Apr	-	.42	.064	.064	.037	.38	-	-	.98	4.0
C. Sample Stored at -4°C.										
Nov 1974	4.03	.42	.061	-	.045	.40	2.15	.025	.57	4.0
Dec	-	.45	.084	-	-	.46	-	-	1.42	3.9
Jan 1975	-	.38	.043	-	.038	.42	2.10	.046	1.15	3.7
Feb	4.03	-	-	-	-	-	-	-	-	-
Mar	-	.42	.063	.064	.043	.40	2.30	.0065	.97	4.2
Apr	-	.42	.061	.062	.036	.41	-	-	1.33	3.9

There are two questions to answer:

1. Is there a change in the chemical composition, as a function of time, at a constant temperature?
2. Is there an optimum temperature at which to store samples until the time of chemical analysis?

We have found that with the exception of PO_4 and Cl, all chemical parameters showed negligible change when stored for seven months at 21, 4 and -4 C. We believe that this is due to the low pH of the solution inhibiting biological growth and losses to the walls by adsorption. In the case of phosphorus the diversity of concentrations is an excellent example of the pitfalls in the analytical chemistry of phosphorus at low concentrations. There are two primary reasons for the diversity of concentration encountered. First, when plastic containers are used, as they were in this case, there can be substantial losses to the walls by adsorption (Annet and D'Itri 1973). Secondly, only molybdate-reactive phosphorus was analyzed, and due to the lability of phosphorus the amount in the molybdate-reactive reservoir changes with time.

The variability of chloride is not as readily explained. There was an increase in the chloride concentration by about a factor of two from the first analysis to the second at all temperatures and the concentrations have remained high. This is indicative of a laboratory error and further work is being done with this element to clarify the situation.

IV. SUMMARY

The following conclusions have been reached about the collection of precipitation for chemical analysis:

1. It is important to use a collector that excludes dry deposition due to its impact on the chemistry of rain and snow.

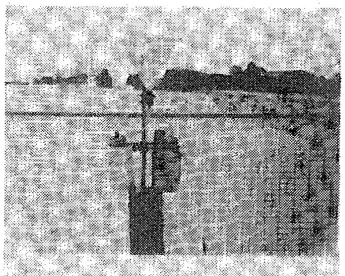
2. If using an automatic collection device, it is necessary that the collector be of rugged design, capable of withstanding long periods in the field. It is recommended that a collector of the type built by the U.S. Atomic Energy Commission be used.

3. For the collection of precipitation for inorganic chemical analysis, it is recommended that plastic be utilized. For the collection of precipitation for organic chemical analysis, it is recommended that glass, stainless steel or aluminum be utilized.

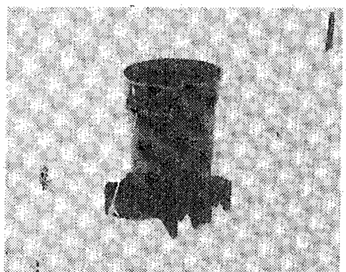
4. For those investigations that require a high degree of accuracy in the determination of precipitation chemistry, it is recommended that samples be collected on an "event" basis, that is, after every storm. In areas where the pH of the precipitation is low (< 4.5) weekly collections are adequate depending on the chemical parameters being analyzed.

5. As a general rule the samples should be analyzed immediately. However, if this is not feasible, our investigations have shown that when the pH of the precipitation is less than 4.5 the storage of samples at 4 C is adequate.

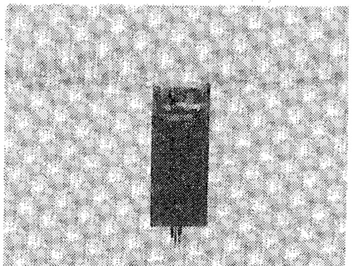
The following figure is a pictorial array of nine of the precipitation collectors used in this investigation.



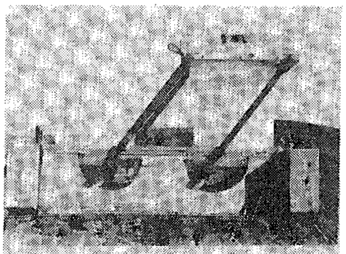
HUBBARD BROOK RAIN COLLECTOR



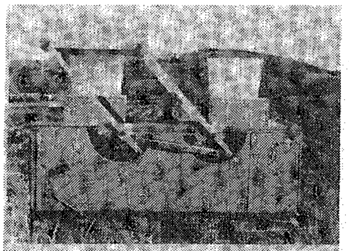
HUBBARD BROOK SNOW COLLECTOR



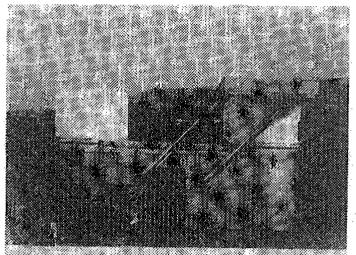
BULK GLASS COLLECTOR



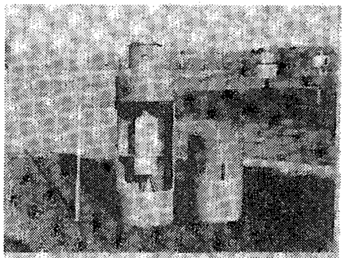
ATOMIC ENERGY
COMMISSION COLLECTOR



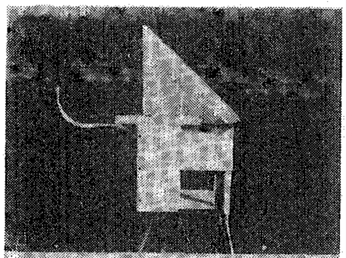
ILLINOIS STATE WATER
SURVEY COLLECTOR



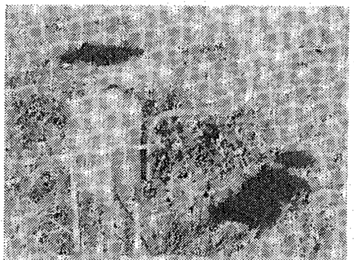
PARELCO OY (FINLAND)



ERNI & CO. COLLECTOR



WONG COLLECTOR



MISCO COLLECTOR

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