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Project Summary

Wet Deposition and Snowpack Monitoring - Final Project Report

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Accurate measurement of snowfall is critical to the assessment of acidic deposition trends, particularly in areas where snow represents 30 percent or more of the annual precipitation. Such areas include the intermountain west, where precipitation amount and, possibly, total chemical loading appear to be correlated strongly with elevation (Svoboda and Olson, 1986). The intermountain area is characterized by complex topography and meteorology, heavy precipitation, and extreme cold. A study was conducted in the spring of 1987 to evaluate equipment performance in complex high altitude terrain. The instruments selected for evaluation included the Aerochem Metrics Model 301 wet/dry deposition collector, the Belfort Model 5-780 weighing rain gage, and the U.S. Geological Survey (USGS)-designed 46-cm bulk samplers. The first two are the standard instruments employed in the National Atmospheric Deposition Program (NADP) and National Trends Network monitoring systems; the bulk sampler is used extensively by USGS in snowfall monitoring studies. All instruments were installed on a platform above the expected snowpack at the University of Denver High Altitude Laboratory, located near Mount Evans in Colorado. Monitoring was conducted between March 5 and June 1, 1987.

Samples were collected on a weekly and event (i.e., individual snowstorm) basis. Collected samples were analyzed for pH, specific conductance, water equivalent, selected metal cations (calcium, magnesium, potassium, and sodium), ammonium, nitrate, sulfate, and chloride. All analyses were performed in laboratory facilities in Las Vegas, Nevada. Instruments were evaluated in terms of interinstrument variability (precision), operational reliability, and accuracy comparison to ground-truth data.

Interinstrument variability was acceptable for most parameters. Between-event variability was most pronounced for pH, specific conductance, nitrate, and sulfate. Operational reliability was excellent for all instruments, although frequent maintenance was required for the Model 301 sampler to ensure free lid movement. The Model 301 sampler lacked sufficient volume capacity for weekly samples or prolonged, heavy events. Both the bulk sampler and Model 301 sampler exhibited acceptable accuracy. Catch efficiency of the Belfort was less than 1/3 to 1/2 that of either the Model 301 sampler or bulk sampler. The low catch efficiency was most pronounced during events of light, low-moisture-content snow, indicating a need for effective windshielding.

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This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings

of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The overall purpose of the project was to assess the suitability of selected collection devices to high altitude, complex terrain situations. This goal was addressed through the following specific project objectives:

1. Estimate interinstrument sampling variability for two colocated Aerochem Metrics Model 301 wet/dry deposition collectors by comparing chemistry and water equivalent for weekly samples.
2. Estimate interinstrument sampling variability for two colocated Belfort weighing rain gages by comparing water equivalent for both weekly and event samples.
3. Estimate interinstrument sampling variability for two colocated bulk samplers by comparing the chemistry and water equivalent for weekly samples.
4. Estimate the accuracy of all collection instruments by comparing the sample chemistry to the chemistry of a ground-truth standard (snow cores). The comparisons include samples collected after events and samples collected weekly.
5. Estimate the accuracy of all collection instruments by comparing the water equivalent of samples to the water equivalent of a ground-truth standard. The comparisons are made on snow core measurements, for both weekly and event samples.
6. Assess operational reliability in qualitative terms of frequency and type of instrument malfunctions, length of downtime, cause and resolution of problems, ease of operation, frequency and ease of maintenance, and evidence of sample contamination.
7. Recommend use of particular instruments and sampling intervals for high altitude, complex terrain situations based on results of the above comparisons.

Participants in the study included the National Acid Deposition Program (NADP), the U.S. Environmental Protection Agency (EPA) Region VIII, the EPA Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV), and the U. S. Department of Agriculture - Forest Service. EPA EMSL-LV and its prime contractor, Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO), had primary responsibility for construction of the monitoring platform, equipment installation, field station operation, chemical analyses, data verification and interpretation, and quality assurance. The monitoring site was located at the High Altitude Laboratory operated by the University of Denver. The High Altitude Laboratory is located adjacent to the Mount Evans Highway near Echo Lake, 14 miles south of Idaho Springs, Colorado. The site offered several advantages: the terrain is complex, the area is subject to large amounts of precipitation and to high winds, the site is accessible year-round, it has electrical power, and it has dormitory facilities. All field operations were conducted between March 5 and June 1, 1987.

Procedure

An octagonal platform was constructed at the site to provide a base above the expected height of the snowpack for the following instruments: 3 Aerochem Metrics Model 301 wet/dry deposition collectors, 2 Belfort Model 5-780 weighing rain gages, and 2 USGS-designed 46-cm diameter flanged bulk samplers. Science Associates Models 424-1 and 424-2 wind speed and wind direction sensors were mounted on a 2-m (approximate) mast in the center of the platform to provide supplementary meteorological data. The Model 301 samplers and the meteorological sensors were interfaced to an IBM-PC data acquisition system (DAS) located in a heated building approximately 70 meters from the platform.

Manual ground-level measurements provided a standard for comparison to the platform-mounted instrumentation. Measurements of snow density were taken in a snowpit. Snowboards provided a base for collection of snow cores to a marker horizon on an event and weekly basis. The snowpit was located in a separate clearing adjacent to the platform; snowboards were located in both clearings.

The monitoring site was serviced by one full-time operator who resided at the site in dormitory facilities leased from the University of Denver. Residence on site allowed for continuous observation of weather and instrumentation throughout the study. Continual observation was vital to accomplishing the project objective of assessing instrument reliability and suitability for snow monitoring in complex, high altitude terrain. The site operator was responsible for instrument checks and calibrati sample collection and shipment, operation, ground-truth measureme and documentation of all field activitie

Samples were shipped weekly to Vegas for processing and analy Processing included determinatio water equivalent, measurement of pH specific conductance, and preparatio aliquots for subsequent analy Analyses, performed every two to weeks, included measurement of cations (calcium, magnesium, potassi and sodium), nitrate, sulfate, chlor and ammonium. A description of sample aliquots and analytical metho presented in Table 1.

Quality assurance (QA) proced were integrated into the field, labora and data operations. Development of quality assurance plan began development of the project plan definition of the specific proj objectives. Each activity was perfor in accordance with written protocols incorporated quality control checks quality assurance/quality control samp

Field and laboratory data w compiled in a single data base on IBM-PC. All data were reviewed compliance with QA/QC objectives to any interpretation of results. Evalua of QA/QC data was completed as were received to identify and rectify problems. Acceptance criteria w applied to audit and blank samp duplicate analyses, and holding times

Verified data were analyzed accordance with the project objecti Comparisons were made of results pairs of the sample collection devi (Belfort rain gages, bulk samplers, M 301 samplers, and duplicate snow co collected over the same sampling pe The mean, range, percent rela standard deviation (%RSD), and anal of variance were computed for w equivalent and chemistry values.

Comparisons between differ instrument models employed statis tests similar to those described above instruments operating over the s sampling interval were compared ba on water equivalent and chemi results. In addition, comparisons w made of same model and different m instruments operating over diffe sampling intervals.

Results and Discussion

Three of the project objecti (numbers 1, 2, and 3) were assessm of variability related to sampling with

Table 1. *Aliquot Descriptions and Analytical Methodologies*

	ALIQUOT 1 - CATIONS
Chemical Parameters	*calcium, magnesium, potassium, sodium*
Aliquot Description	*125-mL Nalgene bottles (acid-washed), filtered (0.45 µm HA type filter), preserved with ultrapure nitric acid to $pH<2$*
Analytical Method	*Atomic absorption spectroscopy[a] (potassium, sodium)* *Inductively coupled plasma emission spectroscopy[a] (calcium, magnesium)*
Maximum Holding Time	*6 months[b]*
Project Holding Time	*4 weeks*
	ALIQUOT 2 - NITRATE AND SULFATE
Chemical Parameters	*nitrate, sulfate*
Aliquot Description	*125-mL Nalgene bottles (not acid-washed), filtered (0.45 µm HA type filter), preserved with mercuric chloride (0.15 M)*
Analytical Method	*Ion chromatography[a]*
Maximum Holding Time	*7 days (nitrate)[c], 28 days (sulfate)*
Project Holding Time	*4 weeks*
	ALIQUOT 3 - CHLORIDE
Chemical Parameters	*chloride*
Aliquot Description	*125-mL Nalgene bottles (not acid-washed), filtered (0.45 µm HA type filter), no preservative*
Analytical Method	*Ion chromatography[a]*
Maximum Holding Time	*28 days[a]*
Project Holding Time	*2 weeks*
	ALIQUOT 4 -AMMONIUM
Chemical Parameters	*ammonium*
Aliquot Description	*125-mL Nalgene bottles (acid-washed), filtered (0.45 µm HA type filter), preserved with ultrapure sulfuric acid to $pH<2$*
Analytical Method	*Flow injection analysis colorimetry[d]*
Maximum Holding Time	*28 days[a]*
Project Holding Time	*2 weeks*

[a] U.S. EPA, 1983

[b] Although the EPA (U.S. EPA, 1983) recommends a six-month maximum holding time for these cations, this study required that all of the cations be determined within 28 days. This was to ensure that significant changes did not occur and to obtain data in a timely manner.

[c] Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (not acidified) be determined within 48 hours of collection, evidence exists that nitrate in mercuric chloride preserved samples is stable for up to three months (Suarez et. al., 1986).

[d] The method for ammonium determination (U.S. EPA, 1983) was adapted for use on a flow injection analyzer at EMSL-LV.

same instrument model. Two aspects of variability were examined in this context: (1) variability between paired instruments of the same type and (2) sampling variability, which is essentially an examination of the effect of each instrument model on system precision. The project objectives specified comparisons between (1) the Model 301 units used to collect weekly samples; (2) the bulk samplers, also used to collect weekly samples; and (3) the Belfort rain gages used for event and weekly cumulative water equivalents. In addition to these specifically stated objectives, interinstrument sampling variability was determined for the Model 301 units used to collect event samples, as was sampling variability in the collection of weekly and event core samples.

The sampling variability measured as percent relative standard deviation (%RSD) of each parameter per sampler was determined by pooling the variance of the sample results for each sampling date and dividing the pooled standard deviation by the grand mean. The residual error term from the analysis of variance (ANOVA) (Steel and Torrie, 1960) gives the pooled variance, which is divided by the grand mean to give a pooled %RSD (coefficient of variation). These %RSD values, presented in Table 2, represent the relative variability of each of the sampling methods used. Snow core data were included in this

Table 2. *Interinstrument Sampling Variability.*

Instrument Type	Ca^{+2}	Cl^-	Corr. Cond.[a]	H_2O EQ[b]	K^+	Mg^{+2}	Na^+	NH_4^+	NO_3^-	pH	SO_4^{-2}
Bulk	9.4	86.5	3.1	1.4	27.3	11.8	19.0	14.1	5.0	0.9	2.7
	8.56*	0.78	0.60	0.0	0.15	1.12	1.86	0.05	0.22	0.31	0.05
	9	10	10	11	10	8	9	11	11	11	11
Model 301	21.1	24.5	4.9	8.7	50.6	17.1	15.8	0.0	3.7	1.0	16.6
weekly	0.65	0.38	0.24	0.93	0.11	0.41	0.03	-	1.15	1.87	0.02
	7	6	7	7	6	7	7	4	7	7	7
Model 301	18.1	46.4	12.6	10.6	7.9	22.7	14.7	6.2	2.9	4.1	3.6
event	4.16	0.05	0.19	0.08	5.63	3.38	3.27	0.24	0.0	0.39	3.01
	6	8	10	10	6	6	3	4	8	10	8
Belforts				7.5							
event				0.39							
				10							
Belforts				5.1							
weekly				5.54*							
				11							
Core	31.1	94.2	72.8	7.9	100.1	54.1	58.2	16.8	14.5	2.9	45.8
weekly	3	5	4	6	3	3	2	3	5	6	5
Core	34.5	14 9	86.9	13.9	24.3	47.5	9.0	33.2	33.6	2.23	15.4
event	4	4	5	5	3	4	3	3	5	4	4

Legend

Line 1 gives instrument precision, expressed as percent relative standard deviation (%RSD).

Line 2 gives the "F" distribution for each parameter per instrument type. An asterisk following the value indicates significance at the 95 percen confidence level.

Line 3 is the total number of sample pairs (n) available for analysis.

[a] *Corr. Cond. = specific conductance, corrected to 25.0°C.*

[b] *H_2O EQ = water equivalent.*

analysis for comparison to the relative variation of the other methods used.

An additional project objective was to investigate possible differences between sampling intervals, specifically by the comparison of Model 301 event and weekly sample results. Two of the three Model 301 samplers were operated on an event basis over a four-week period; the remainder of the time, two samplers were operated weekly. Sampling interval differences were also investigated for event and weekly snow core samples. Event snow cores were collected over the same four weeks that two Model 301 samples were collected on an event basis. Snow core data were deleted from the data base during verification because the samples they represented were contaminated or affected by evaporation, melting, wind scour, or sublimation. These deletions resulted in an insufficient number of sample data remaining to permit an accurate assessment of variability due to differences in sampling intervals from snow cores. Although both event and weekly data are available for Belfort rain gages, the weekly data were derived by cumulation of event data and are, therefore, not independent.

Water equivalent comparisons were made by adding individual event data and comparing the result to the weekly sample water equivalent. Two events were collected during the first week of event sampling. The weekly sample and the event-cumulative water equivalent for one of the event samplers were equal (1.06 cm); the second event-cumulative was approximately 20 percent less. Only one event occurred in the second week; water equivalents for both event samplers were within 10 percent agreement with each other and with the weekly sample. The weekly sample was the lowest of the three values. A total
seven events were collected in the th
week. Both of the event-cumulat
water equivalents were greater than t
of the weekly sample; one was about
percent greater while the other was
percent greater. The two eve
cumulatives were within 7 percent
each other. During the last week of ev
sampling, two events were collected.
event-cumulatives were equal (2.
cm); the weekly sample was 25 perc
greater. The weekly sample for this
week, however, included snow from
event which occurred on the day
collection, and the snow from that ev
was not included in the event samples
general, the event-cumulatives were
close agreement with each other and w
the weekly sample.

Instrument reliability as a function
low maintenance and high sam
recovery was determined from dir

observation of instrument operation by he field operator and through verification of sample loss or contamination. The Model 301 samplers required the most time for operational maintenance. Over the first two weeks of sampling, the wet buckets in each unit were replaced three times a week to ensure complete sample collection. During the event sampling period one particularly heavy snowstorm required four bucket replacements. The Model 301 samplers also required snow removal during snowstorms from the peaked roofs and from the lid arm joints to maintain lid mobility. The only maintenance required for the bulk samplers was a daily visual check of fill heights. Maintenance of Belfort rain gages included daily clock and pen inspections, replacement of the antifreeze-oil mixture every 2-4 weeks, and monthly calibration checks.

Two of the project objectives (Objectives 4 and 5) were to evaluate the accuracy of the platform-mounted instruments by comparing water equivalent and chemical data to the data produced by ground-truth measurements. Comparisons were made between ground-truth measurements and weekly Model 301, bulk, and Belfort samples, and event Model 301 and Belfort samples. The ground-truth measurements were selected to be the standard for comparison because these methodologies have been commonly employed in classic snowpack studies. A completely randomized design (CRD) analysis of variance (Steel and Torrie, 1960) was used to test the differences between the means of snow core data and the means of platform-mounted instruments.

The CRD model used is:

Source of Variation	Degrees of Freedom
Random error	1
Residual error	n-1

where,

n = number of pairs of data collected

The null hypothesis in this case is:

There are no differences between ground-truth measurements and measurements taken by the platform-mounted instruments.

F-values were significant at the 95 percent confidence level for all comparisons of magnesium, potassium, and chloride. Additionally, event sample F-values were significant at the 95 percent confidence level for specific conductance, pH, calcium, and sodium.

The number of significant differences found between platform-mounted instruments and ground-truth measurements does not necessarily indicate a high degree of inaccuracy in the platform-mounted instruments. In this study, the snow accumulations on snowboards were scraped whenever volume was insufficient for coring. Analysis of the scrapings produced little usable data because of sample contamination and the high imprecision of the results that was caused, in part, by the small number of routine/duplicate pair data remaining after data verification. Additionally, weekly snow core and snow scraping data are suspect due to observed sample loss by evaporation, melting, wind scour, and sublimation. Finally, the snow cores are most directly comparable to bulk samplers as both are exposed to both wet and dry deposition. The cores are less comparable to the Model 301 samplers since the sampler lid serves to separate wet and dry deposition.

Because of the poor results obtained in this analysis and the suspicion that the snow core data were questionable, an additional analysis was conducted. In this analysis, the results obtained from the platform-mounted instruments were compared to each other. This analysis provides an indication of comparability among the tested collection methods. The data indicate that the water equivalents measured by the Belfort were consistently lower than those measured by either the bulk or Model 301 samplers. Belfort sample values ranged from only slightly lower than other sample values when wet snow events were collected to less than 50 percent collection for dry snow events. This circumstance was probably caused by air turbulence created by the Belfort sampler itself. Alter windshields were not used on the Belfort units because evidence exists that they are not effective at windspeeds greater than 3mph (Goodison et al., 1981; Goodison and Metcalfe, 1982). The low catch efficiencies observed in this study, however, indicate that some effective type of windscreen is needed if Belfort rain gages are to be used to collect snowfall.

Comparison of the analytical results for Model 301 samplers and the results for bulk samplers indicated the values were statistically the same for every parameter measured. The bulk sampler is exposed to both wet and dry deposition while the Model 301 sampler has a lid which prevents dry deposition from entering the wet bucket. The results of this analysis indicate that, at least for this study, dry deposition was not a significant factor.

Conclusions and Recommendations

The Belfort rain gage did not perform well in this study. While interinstrument precision was acceptable, comparisons to the bulk and Model 301 samplers as well as to event snow cores indicated a very low catch efficiency by the Belforts. Catch efficiency was lowest during dry snow events, indicating the problem is likely due to wind turbulence and, possibly, could be corrected by addition of an effective windscreen. Additional disadvantages noted for the Belforts included snow accumulation in the funnel and excessive pen vibration. The first was resolved by addition of heat tape which was manually activated during snow events. The pen vibration is likely to be a problem any time platforms are used. Finally, the rain gage produced only water equivalent data; chemical analyses were precluded by the use of an antifreeze-oil mixture in the collection bucket. For these reasons, the rain gage as presently configured cannot be recommended for snow collection in high altitude, complex terrain.

The coring methodology, while appropriate to classic snowpack studies, is not appropriate to short interval monitoring. Snow accumulation for a single event or weekly period was often insufficient for cores. Compositing of multiple cores or area scrapings as done in this study increases the contamination risk. As an alternative, collection of snowfall from clean plastic sheets placed on the snow surface might be preferable.

The Model 301 sampler performed satisfactorily. Both interinstrument and intermodel precision were acceptable for most parameters. No samples were lost due to contamination. The voltage output of the lid arm mechanism provided data on the start, end, and duration of events. The moisture sensors of the three units were observed to respond individually to the onset and end of events, but this variability did not appear to affect the interinstrument precision significantly. Modification of the sensor improved detection sensitivity. A similar sensor is available from the manufacturer. The major disadvantages of the Model 301 sampler are: (1) extensive maintenance is required to ensure operational reliability and (2) bucket capacity is insufficient for heavy snow events or prolonged sampling intervals. Both disadvantages are likely to be problems in any unattended operation in heavy snowfall areas.

The bulk sampler also performed satisfactorily. The bulk sampler required no maintenance apart from collection bag changes, and bag volume was more than sufficient for weekly sampling. Additionally, the bulk sampler does not require electrical power, thus permitting location in remote areas.

Some disadvantages of the bulk samplers were noted. The bags supplied by GSA became brittle at low temperatures and occasionally leaked; use of a different material is recommended, and strength and temperature testing should be performed before utilizing bags of a new material. The bulk sampler is open to the atmosphere at all times; therefore, it is subject to dry deposition, and the risk of contamination is somewhat greater than for the Model 301 sampler. However, interinstrument precisions obtained in this study were nearly equivalent to those obtained by the Model 301 sampler; comparisons between the bulk and Model 301 samplers indicated statistically equivalent measurements of all parameters. Therefore both the Model 301 sampler and the bulk sampler can be recommended for snow collection.

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The complete report, entitled "Wet Deposition and Snowpack Monitoring – Final Project Report," (Order No. PB 88-165 717/AS; Cost: $19.95, subject to change) will be available only from:

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