United States
Department of
Agriculture

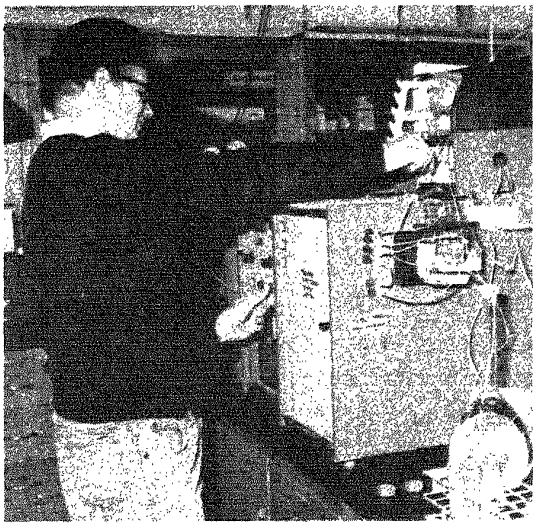
Forest Service

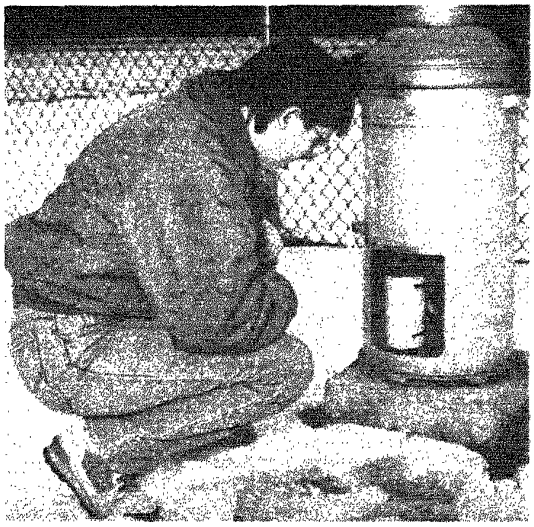
**Northeastern Forest
Experiment Station**

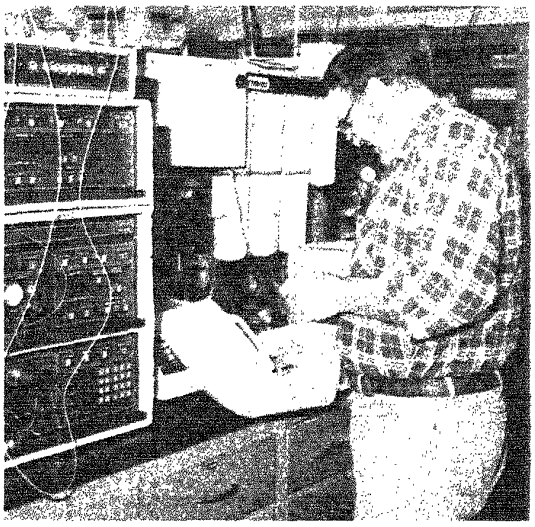
General Technical
Report NE-177

Field and Laboratory Quality Assurance/Quality Control Protocols and Accomplishments for the Fernow Experimental Forest Watershed Acidification Study

Pamela J. Edwards
Frederica Wood







Abstract

Field and laboratory quality assurance/quality control (QA/QC) protocols for a whole-watershed acidification study on the Fernow Experimental Forest are described. Procedures are detailed thoroughly to: (1) allow individuals familiar with QA/QC to judge for themselves the quality and suitability of the protocols and resulting study data, and (2) provide sufficient information that will enable readers who are considering QA/QC implementation to set up a reasonable program. Accomplishments are quantified in terms of several test criteria to present the QA/QC results specific to this study and to illustrate typical results that can be expected from a relatively rigorous QA/QC program.

The Authors

PAMELA J. EDWARDS and FREDERICA WOOD are hydrologist and computer programmer analyst, respectively, with the Northeastern Forest Experiment Station's Timber and Watershed Laboratory at Parsons, West Virginia.

Manuscript received for publication 7 January 1993

Northeastern Forest Experiment Station
5 Radnor Corporate Center
100 Matsonford Road, Suite 200
P.O. Box 6775
Radnor, Pennsylvania 19087-4585

May 1993

Introduction

In 1987, the USDA Forest Service and the U.S. Environmental Protection Agency began a cooperative study on the Fernow Experimental Forest in north-central West Virginia to attempt to artificially acidify a watershed by elevating nitrogen and sulfur inputs using ammonium sulfate fertilizer. Experimental methods included a paired watershed approach whereby one watershed was treated with the ammonium sulfate and another retained as a control. Helicopter applications were made three times per year so that annual nitrogen and sulfur inputs from the fertilizer were approximately twice those in ambient bulk deposition. Responses of stream water and soil leachate chemistry to treatment were the principal parameters studied.

The results of those chemical responses are detailed in several papers, including Edwards and Wood (1992), Strickland and Wildensee (1990), Wildensee and Strickland (1990), and Edwards and Kochenderfer.[1] The purpose of this paper is to describe the extensive quality assurance/ quality control (QA/QC) procedures and protocols implemented to maximize data quality. QA/QC accomplishments are quantified to provide the reader with information about data quality in reference to other publications about this study.

Field Procedures

Electronic Equipment Housing Protocols

Stream monitoring equipment (except stage recorders) was housed in shelters described in Kochenderfer and Edwards (1990). The shelters were positioned directly over each stream at the point where monitoring and sampling were performed. Storm samples were collected and in situ monitoring was performed beneath a door in the shelter floor. Consequently, rain gear, from which precipitation could drip and contaminate samples, was removed immediately upon entering a shelter. Mud, leaves, and other debris were cleaned from shoes before entering. Each shelter was cleaned at least quarterly and more frequently if necessary.

The door in the floor was kept closed from April through October to reduce sunlight and heat reaching the stream water. This procedure maintained the stream water in a more natural condition and minimized the buildup of algae on the pH electrodes and conductivity cells. The door was kept open from November through March to allow warm air to circulate and so prevent stream water from freezing and damaging the electrodes measuring in situ pH.

Water that was sampled and monitored was held temporarily in a plastic tub beneath each shelter. About 3 days after each ammonium sulfate application, the tub on the treated watershed was cleaned so that all fertilizer applied directly to the stream and held in the tub was removed; thus, the quality of subsequent data was not jeopardized. Tubs on both the treated and control watersheds were cleaned when sediment became 1 to 2 inches thick.

In Situ Stream Monitoring

An electrochemical instrument called a Minimonitor[2] obtained from the U.S. Geological Survey was used to continuously monitor in situ stream pH, electrical conductivity, and temperature from both watersheds. Each Minimonitor was connected to an Omnidata Easy Logger data logger. Digital readings from each Minimonitor were transferred electronically to a data storage pack (EPROM) on the data loggers.

Minimonitor and data-logger operations were checked every Monday and Thursday to maximize data completeness and integrity. During these checks, the storage packs were replaced with blank packs, and the calibrations of the conductivity cell and pH electrodes were tested.

The solution for checking the calibrations of both the conductivity cells and pH electrodes was prepared in the laboratory by placing 0.10 ml 1 N H_2SO_4 in a 1-L volumetric flask and bringing it to volume with deionized water. This solution had a conductivity of 42.1 $\pm$ 5 μS cm^{-1} and a pH of 4.00 $\pm$ 0.1. Following preparation of each new liter of solution, the conductivity and pH were tested in the laboratory to ensure that both readings were acceptable.

In the field, calibration of the conductivity cells was tested first. The temperature probe was used during the conductivity check to correct for the solution temperature. The conductivity cell and temperature probe were rinsed with the prepared solution before a reading was taken; then the conductivity of a clean aliquot of solution was measured and recorded on a field data sheet. The cell was rinsed with distilled water before being returned to the stream water.

The performance of a pH electrode was tested next. Each Minimonitor had two pH electrodes; only one of the two pH electrodes was tested during each visit, alternating the one that was tested each Monday and Thursday. The pH electrodes required minutes to hours to recover from testing depending on stream temperature and electrode age, so alternating electrodes assured that at least one would be operational if a storm event occurred soon after a site visit.

---

[1] Edwards, Pamela J.; Kochenderfer, James N. Artificial watershed acidification on the Fernow Experimental Forest. In preparation.

[2] The use of trade, firm, or corporation names in this paper is for the information and convenience of the user. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture or the Forest Service of any product or service to the exclusion of others that may be suitable.

In summer, before testing, the glass bulbs and the end of the pH electrodes were cleaned with a moist cotton swab to remove algal accumulations that formed easily during the warm months and became problematic during low flows. The pH electrode was rinsed with the prepared solution before a reading was taken, and then immersed in clean solution so that a pH reading could be obtained and recorded. The electrode was rinsed with distilled water before being returned to the stream.

The combination of the previous and current pH or conductivity readings was used to determine the need for recalibration of pH electrodes or conductivity cells, respectively. If a current reading was far outside of the acceptable range for the QC check, the electrode or cell was recalibrated the same or following day. If the electrode or cell was only slightly out of the acceptable range and the previous reading was not near the outer limits of acceptability, recalibration was delayed at least until the next visit's reading was obtained. This procedure was necessary because the electrodes often zeroed in on the exact buffer readings even though they were only slightly out of calibration. This occurred due to the high ionic strengths of the buffers used. If both previous and current QC check readings were out of range, recalibration was performed either the day of the second reading or the next day. The pH electrodes were replaced when they consistently lost their calibration between weekly QC checks. Conductivity cells and temperature probes were replaced only when they were damaged physically.

Calibration of the conductivity cells generally was necessary only during the fall and spring when stream temperatures underwent sudden changes. The cells were rinsed and then calibrated with a laboratory-prepared 0.0005 N KCl solution (0.03725 g KCl dissolved in 1 L deionized water) with a theoretical conductivity of 73.9 $\mu S\ cm^{-1}$. However, the value of the prepared solution was determined in the laboratory, and the Minimonitor was calibrated using the laboratory reading rather than the theoretical value.

More frequent recalibration of the pH electrodes was necessary, about every 3 to 4 weeks for each electrode. Recalibration was performed using laboratory-grade pH 7.00 and 4.00 buffers. The electrodes were cleaned with a cotton swab before recalibrating during the summer to remove algae and other dirt which might have accumulated and possibly altered the calibration. Each electrode was rinsed with distilled water and the appropriate buffer before calibration, and again with distilled water before being returned to the stream.

The calibration of the temperature probes was not checked routinely. Testing was done only after Minimonitor maintenance; calibration boxes supplied with the Minimonitors were used. Stream temperature records were examined following each downloading session to ensure that data were reasonable and that there were no anomalous readings.

Normally, testing and calibration of conductivity cells and pH electrodes were not performed during storm events to avoid unnecessary loss of data during the recovery periods. Some testing and calibration during storms were conducted at the beginning of the study until we realized that recovery times were variable and could be lengthy.

Recovery periods for the conductivity cells were rapid, usually requiring less than 20 minutes. The recovery was considered complete when the conductivity reading returned to within 0.2 $\mu S\ cm^{-1}$ of the reading just before the check was performed; if the probe was calibrated, recovery was considered complete after the reading remained stable for 30 minutes.

By contrast, pH recoveries required a much longer time depending somewhat on stream temperature, electrode age, and whether the electrode had been in contact with the low ionic-strength solution or high ionic-strength pH buffers. Low temperatures and high ionic-strength buffers prolonged the recovery periods. Recovery was considered complete when the pH reading returned to within 0.05 unit of the pretest reading. However, if algae were growing on the glass bulb before testing or the probe required calibration, the initial pH generally was inaccurate. In those cases, the initial pH was not used to determine the point of recovery. Instead, recovery was considered complete after the pH reading remained stable for 30 minutes.

For both conductivity and pH, data that were logged during the recovery period were not included in the final data set.

Minimonitors were powered by 12-volt marine batteries attached to solar panels. Data loggers also were powered off the 12-volt battery and had internal D-cell battery backup. The charge on the 12-volt battery was checked during each site visit using a display option on the Minimonitor and data logger. When the charge dropped below 11.5 volts, the battery was replaced.

Stormflow Sampling Protocols

Stormflow samples were collected from the streams using ISCO sequential samplers. They were powered by 12-volt marine batteries. During each site visit, the battery charge was checked with a volt meter. When the charge dropped below 12 volts, the battery was replaced.

ISCO cases containing clean polyethylene bottles were placed in the field every week. Normally, bottle lids were removed at the time the ISCO bases were installed because storms were frequent and unpredictable. However, if long, dry periods were predicted, lids were not removed until a storm was forecast. Disposable vinyl gloves were worn when lids were removed. Lids were placed in clean plastic bags and sealed with a wire twist-tie. Bags were stored in the middle of the ISCO cases.

If lids were removed at the time the bottles were placed in the field and no storm was sampled for the week, a clean base was installed at the end of the 7-day period. No uncapped bottles were kept in the field longer than 7 days to reduce the potential for contamination.

ISCO bases containing clean bottles replaced bases containing samples collected earlier during storms. When the samples were collected, bottles were recapped by workers wearing clean gloves. A field blank was prepared at this time. Distilled water was dispensed into a clean ISCO bottle using the same handling procedures used for regular samples. One field blank was collected for each ISCO case. Field blanks were placed in the middle of the cases and transported to the laboratory.

Streamflow Measurement Protocols

Streamflow was monitored continuously using 120° V-notch weirs in combination with FW-1 water-level stripchart recorders. Stripcharts were changed every Tuesday and read quarterly with a digitizer. The accuracy of the readings was evaluated by comparing the readings with streamflow and rain-gage results from surrounding watersheds. When incorrect flows were identified, corrections were made to the charts based on neighboring watershed streamflow charts.

Stream Grab-Sample Protocols

Stream water was grab sampled every Tuesday from permanently marked locations near the mouth and at two headwater sites on each watershed. The sample bottles and caps were rinsed three times with stream water before samples were collected. Neither the streambed nor stream water upstream from the collection sites was disturbed before the sample was collected to avoid altering its chemistry.

One field blank also was collected, alternating between the two watersheds each week. Distilled water was dispensed into a bottle identical to that used to take the grab sample. The handling procedures used were the same as for the grab samples. Once each quarter, a duplicate grab sample was collected at each stream sampling location. All grab samples were stored in a cooler during transport to the laboratory.

Throughfall and Precipitation Protocols

Throughfall was collected at 20 locations on the control watershed to obtain estimates of ambient bulk-deposition levels. No throughfall samples were taken on the treated watershed to avoid contaminating samples during and after applications of fertilizer.

Each location for throughfall sampling was permanently marked with a piece of rebar onto which the throughfall collectors were clamped. Throughfall was collected in 8-inch-diameter polyethylene funnels which drained down into 2-L polyethylene flasks. The flasks and funnels were clamped near the top of the rebar, with the top of each funnel above the rebar and clamps to avoid contamination from splash, and approximately 1.2 m above the ground. Looped Tygon tubing, which minimized sample evaporation, connected each funnel and flask.

Throughfall was collected only during the growing season because snow-bridging across the funnel during the dormant season made accurate sampling impossible. During the growing season, samples were collected each Monday, at which time the entire collector (i.e., funnel, flask, and tubing) was replaced with a clean one. A 2- by 2-inch fiberglass swab was inserted into the base of each clean funnel using stainless steel tweezers and disposable gloves. The swabs minimized the amount of debris, such as twigs, leaves, and insect frass that washed into the flasks.

Bulk and wet precipitation were collected every Tuesday from a weather station located in the head of the control watershed. Wet precipitation was collected with a solar-powered Aerochem Metrics automatic precipitation collector. The collector was equipped with a propane heater during the winter so that the instrument remained operational during freezing conditions. The wet-side bucket was replaced with a clean bucket using the procedures outlined by the National Atmospheric Deposition Program (NADP) (Bigelow and Dossett 1988). The moisture sensor was tested at the time the bucket was changed to ensure proper operation.

Bulk precipitation was collected in a funnel and bottle combination from May 1 to October 31 and with an open bucket from November 1 to April 30 in a rain-gage opening near the ridgetop of the control watershed. Precipitation collectors were similar to the throughfall collectors except that a 1-L polyethylene bottle was substituted for the flask, and no fiberglass swab was used in the funnel. The bottle and funnel were clamped to a pole at an approximate height of 5 m to minimize disturbance by black bears. To avoid snow-bridging across the top of the sampler during the dormant season, a bucket positioned approximately 1 m above the ground in a wooden stand was used. The bottle and funnel assembly or bucket was replaced each Tuesday.

Total precipitation for the 7-day period was obtained from a standard nonrecording 8-inch rain gage. Daily totals and intensities were determined from a weighing-type recording rain gage with stripchart. The stripchart from the recording rain gage was changed weekly and read quarterly. Precipitation from both gages was compared to that from other rain gages on the Fernow Experimental Forest to ensure that values were similar and, therefore, reasonable. Adjustments were made to the charts using neighboring watershed precipitation charts when readings were deemed inaccurate.

Lysimeter Protocols

Zero-tension lysimeters were used to collect samples of soil water produced by gravity drainage. Consequently, flow into the 4-L sample collection bottles was not easily predicted, so the contents of several representative bottles were checked weekly during wet periods and monthly during dry

periods. Bottles were retrieved when approximately 20 lysimeters per watershed contained at least 1 L, but before the sample overflowed. No microbial inhibitors were used in the sample bottles to avoid possible contamination of a downstream municipal water supply. All bottles were replaced at the time of sample collection even if they contained no sample. The amount of overflow in the buckets, if any, was recorded but not sampled since the buckets were not cleaned or replaced. All overflow was discarded downslope of the lysimeters so that it was not recycled through the lysimeter system.

Two field blanks were taken on each watershed, one at a lysimeter near the mouth and head of each when lysimeters were collected. Approximately 1 L of distilled water was dispensed into a clean bottle identical to the lysimeter bottles. The same handling procedures were used for the field blanks as the lysimeter samples.

Once per quarter, duplicate samples were taken from 25 percent of the lysimeter samples. Sample division into duplicates was performed in the laboratory.

Sample Identification

All water samples (including field blanks) were identified by a batch and sample number. Every batch number was unique and was stamped onto field forms with a Bates Numbering Machine to assure that no number was repeated within the same year. Specific sample details and remarks were recorded on the field forms. ISCO bottles were permanently identified with a three-digit sample number and a watershed number. Bottles designated for a specific watershed were used only on that watershed to minimize the potential for cross-watershed contamination. As ISCO cases were loaded with bottles before transport to the field, the sample bottle number was recorded according to its appropriate sample position in the case (1 to 24). The field form (with pre-labeled batch number) was placed in the center of the ISCO case and retained with the case at all times until it was returned to the laboratory.

All grab samples were labeled with a batch and sample number in the field at the time of sample collection. Lysimeter, precipitation, and throughfall samples were labeled with a batch and sample number in the laboratory after volume was determined. The description of each sample was recorded on a field form that differed from the ISCO form.

Field batch forms for ISCO samples were numbered from 500 to 999; those for grab samples, lysimeters, precipitation, and throughfall were numbered from 001 to 499. This separation of numbers provided the laboratory staff with information on sample priority. Generally, storm samples from the ISCOs were given priority for analyses because of the objectives of the study.

Field blanks were labeled and added to the batches as samples. Field forms were not made available to the analytical laboratory staff to reduce the tendency toward biasing results. ISCO batch numbers were provided to the laboratory employee processing samples since batch numbers were not recorded on the bottles. The dates of collection for each batch were retained by the laboratory staff so that samples were analyzed within approved holding times.

Laboratory Procedures

Preparation of Sample Bottles

All collection devices (e.g., bottles, caps, funnels, etc.) were washed with warm water and laboratory-grade soap, rinsed with tap water, and rinsed again with distilled water that had been passed through a mixed-bed demineralizer cartridge (Barnstead D8902). The laboratory's deionized water system could not meet the large weekly sample load demands, and the electrical conductivity of the cartridge-treated distilled water was nearly identical to that of the deionized water. As a result, distilled water was judged adequate to use for rinsing.

When cleaning was completed, the bottles were divided into groups of approximately 20. Distilled water was placed in a randomly selected bottle from each group for approximately 24 hours, after which time electrical conductivity was measured. If the measurement was less than 2 $\mu S\ cm^{-1}$, the batch of 20 bottles was considered clean. If a test bottle failed the conductivity test, the 20-bottle group was rerinsed with distilled water and a second conductivity reading was taken 24 hours later. A second failure resulted in rewashing the group of bottles in question and checking for a source of contamination within the distilled-water system. Results of all bottle testing were recorded in a notebook.

Sample Preparation and Analyses

Samples brought to the laboratory were prepared for analysis within 24 hours. Sample volumes for lysimeters, wet and bulk precipitation, and throughfall were determined gravimetrically. Tare weights for the sample containers were recorded permanently on the containers so they did not have to be reweighed after emptying.

The accuracy of the balance used for weighing samples, as well as all other balances, was checked prior to each period of use with an ANSI class 1 weight. If the reading was not correct, the balance was recalibrated. Results of each balance check or recalibration were recorded in a notebook.

Approximately 250 ml of each sample were vacuum-filtered through 0.45-μm membrane filters. The filtered portion was divided into six aliquots and preserved and analyzed by the methods given in Table 1. Another 250 ml were kept unfiltered and unpreserved for pH, electrical conductivity, and alkalinity or acidity determinations. Analyses were completed, assuming no instrument malfunctions or unusual situations, within EPA-approved holding times (Table 1).

Archives for each analyte were retained after analyses until all quality assurance tests (described later) and reanalyses, if required, were completed. The original aliquot remaining after initial analysis for each analyte except the anions were archived.

Because the initial 5-ml anion aliquot was placed in an autosampler vial, a separate 50-ml archive aliquot was prepared when the samples were filtered. For all analytes, the archived samples were stored in the same manner as for the initial analysis. For most samples what failed quality assurance tests, sample holding times usually were exceeded by the time reanalyses were completed. These violations were noted by flags in the data files (described later).

Table 1.—Preservation methods, instrumentation, and holding times for each analyte

Aliquot	Preservation	Instrumentation	Holding time	Remarks
Filtered			Days	
DOC	Acidify to pH2 with H_2SO_4 Store at 4°C	Dohrmann carbon analyzer	14	Same aliquot used for DOC and NH_4
NH_4	Acidify to pH2 with H_2SO_4 Store at 4°C	Wescan ammonia analyzer	7	
Ca, Mg	Acidify to pH2 with HNO_3 Store at room temp	Perkin Elmer 503 atomic absorption spectrophotometer	56	LaCl added to aliquot before analysis
Na, K	Acidify to pH2 with HNO_3 Store at room temp	Perkin Elmer 503 atomic absorption spectrophotometer	56	
Cl, NO_3, SO_4	Store at 4°C	Dionex 4000i ion chromatograph	7	
Anion archive	Store at 4°C			
Unfiltered				
pH	Store at 4°C	Fisher 915 pH meter with combination electrode	7	
Electrical conductivity	Store at 4°C	Radiometer CDM83 conductivity meter with platinum cell	14	
Alkalinity or acidity	Store at 4°C	Radiometer VIT90 video titrator	14	

Quality Control

All laboratory instruments were calibrated according to the manufacturer's recommendations at the beginning of each day's use. Calibrations were checked throughout the day using quality-control check samples (QCCS) of known concentrations. A QCCS was analyzed immediately after the calibration, following every 10th sample, and at the end of each batch, with a minimum of three QCCS analyses per batch. If a QCCS fell outside of the acceptable control limit range (Table 2), the instrument was recalibrated and all samples since the last QCCS were reanalyzed. The ion chromatograph (IC), atomic absorption spectrophotometer (AA), carbon analyzer, and ammonia analyzer calibrations also were checked immediately following each calibration with standards near each respective instrument's high and low ranges. To be acceptable, the high and low standard concentrations had to be within specified control-limit percentages (Table 2); if any standard fell outside those limits, the instrument was recalibrated. All new standards and QCCS were analyzed three times before use to ensure accuracy.

Dynamic range and detection limit tests were performed near the beginning of each quarter on the ion chromatograph, atomic absorption spectrophotometer, and the ammonia analyzer. The test results were used to identify sample and QA/QC data outside of acceptable concentration ranges. Sample concentrations above the upper concentration of the dynamic-range test required dilution and reanalysis. Sample concentrations below the low detection limit for each analyte were flagged and not included in the final data set

For the dynamic-range tests, a regression curve was fitted to a set of standards covering the expected concentration range of samples. The AA and IC had nonlinear calibration curves (second-order polynomial), while the ammonia analyzer had a linear calibration curve. A minimum acceptable R^2 value of 0.90 was required, though an R^2 of 0.95 or greater usually was obtained. Concentrations at either end of the curve were eliminated as necessary to obtain a good fit; however, accuracy and curve fit were considered when defining the upper and lower curve range. Typically, any shifts in the range tests occurred at the lower concentrations.

Table 2.—Specifications for acceptable quality control check samples (QCCS) results

Analyte	Known QCCS concentration	Worst-case control limit (+/−)	Measured limit[a]	
			Lower	Upper
		Percent		
DOC	2.00 mg C L^{-1}	10	1.80	2.20
Ca	1.00 mg L^{-1}	5	0.95	1.05
Mg	1.00 mg L^{-1}	5	0.95	1.05
Na	1.00 mg L^{-1}	5	0.95	1.05
K	1.00 mg L^{-1}	5	0.95	1.05
NH_4	0.40 mg L^{-1}	10	0.36	0.44
Cl	0.50 mg L^{-1}	10	0.45	0.55
NO_3	0.50 mg L^{-1}	10	0.45	0.55
SO_4	3.25 mg L^{-1}	5	3.09	3.41
pH	4.00	2	3.92	4.08
Electrical conductivity	42.1 μS cm^{-1}	5 μS cm^{-1}	37.1	47.1

[a]Units are same as QCCS concentration units.

The standard of lowest concentration included in the dynamic-range test curve was used to determine the low detection limit for each analyte and the maximum concentration of any analyte permissible in a field blank. The lowest possible detectable concentrations (i.e., the detection limit) of the AA, IC, and ammonia analyzer were defined as 3 times the standard deviation of 10 replicate analyses of the low-end concentration standard determined in the range test. The highest permissible concentration of an analyte in a field blank was defined as 2 times the detection limit. Field blanks with concentrations greater than this amount for any analyte were flagged for contamination at the time of data validation and verification. Field-blank conductivities greater 2 μS cm^{-1} also were flagged for contamination.

Data Validation And Verification

Once sample analyses were completed, laboratory results were transferred to the data manager for data entry and verification and validation. Data were checked for mistakes and corrected as necessary before further validation. Following entry and correction, data were checked for violations of holding time. If any occurred, a holding-time flag was inserted into the computer data file.

The correctness of analyses was checked next using anion-cation balances and electrical-conductivity balances. Concentrations were converted from mg L^{-1} to μeq L^{-1} for ion balance checks. The percent ion difference between the sum of all anions and all cations was determined using:

$$\% \text{ Ion Diff} = \frac{(HCO_3 + Cl + NO_3 + SO_4) - (Ca + Mg + Na + K + NH_4 + H)}{(HCO_3 + Cl + NO_3 + SO_4 + Ca + Mg + Na + K + NH_4 + H)} \times 100$$

Acceptable percent differences were those defined by Peden (1981) and varied with the total ionic strength of the solution (Table 3).

The percent ion difference was calculated only for samples for which alkalinity was measured—principally stream samples. Samples for which acidity was determined could not be translated to a measure of bicarbonate, so the calculation was not performed. The calculation could have been made had acid neutralizing capacity (ANC) rather than acidity been measured (U.S. Environ. Prot. Agency 1987).

If the percent ion difference was outside the limits of acceptability, each analyte was examined and compared to other samples taken earlier or to the historical range. Individual analyte outliers identified in this manner were subject to chemical reanalysis of the appropriate archived aliquot. If no obvious outlier could be identified among the individual analytes, the sample was flagged as being outside of the acceptable range but still included in the data set since each analyte concentration was found to be reasonable.

To test data for accuracy using electrical conductivity as a criterion, concentrations expressed as μeq L^{-1} were converted to equivalent conductivities using equivalent ionic conductivities extrapolated to infinite dilution in aqueous solutions at 25°C for each analyte (Weast 1988). The sum of the equivalent conductivities of all analytes for each sample was calculated, and percent conductivity difference was calculated by:

$$\% \text{ Cond. Diff.} = \frac{\text{Calculated Cond.} - \text{Measured Cond.}}{\text{Measured Cond.}} \times 100$$

Again, this calculation was performed only for stream samples since a determination for bicarbonate was not available.

If the percent conductivity difference was outside of the acceptable range shown in Table 3, sample evaluation and reanalysis followed the process shown in Figure 1. Conductivity comparisons to previous samples were made either to previous weeks' samples, in the case of grab samples, or to earlier samples in the same storm for stormflow samples. The majority of conductivity checks that initially failed followed the most right-hand path in Figure 1.

Table 3.—Ion balance and electrical conductivity test criteria for identifying samples that must be reanalyzed

Ion Balance	
Total ionic strength (μeq L^{-1})	Maximum % ion difference
< 50	60
≥ 50 < 100	30
≥ 100	15
Electrical Conductivity	
Measured conductivity (μS cm^{-1})	Maximum % conductivity difference
< 5	50
≥ 5 < 30	30
≥ 30	20

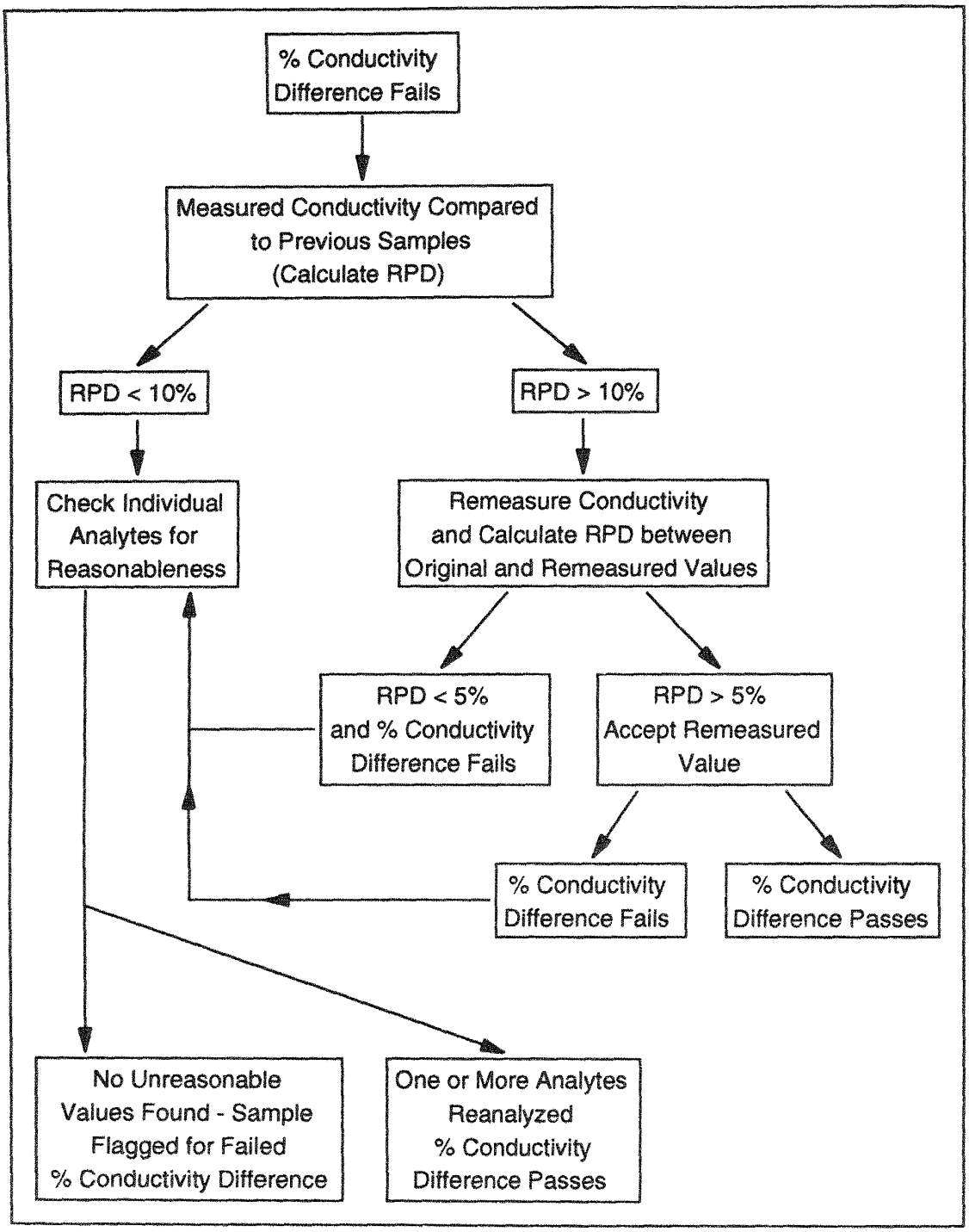


Figure 1.—Procedures followed for samples that fail the test for percent conductivity difference.

A final check for anomalous data was made visually. Data were plotted over time and examined for unusual concentrations. This method was particularly useful for stormflow chemistry data, which generally followed a common pattern. Outliers were identified and retained in or deleted from the data set after considering factors that may have influenced the data point, for example, precipitation patterns or flow. An outlier that was extreme and could not be explained by other factors was deleted from the master data file. Data deletion was done only rarely and with great care.

Data collected electronically from the Minimonitor were downloaded to a personal computer. Data logged from temperature probes during site visits were flagged, but because the readings returned to normal almost immediately after probes were replaced into the streams, no other flags were required.

Conductivity values were flagged during and for a short time after the visit (usually less than 1 hour). Conductivity data were flagged until the conductivity returned to within 0.2 μS cm^{-1} of the pre-visit value. In the summer when algae accumulated, data were flagged until a stable reading was maintained for about 30 minutes following the site visit.

Minimonitor pH values were flagged during site visits for the electrode that was checked or calibrated; it often returned to pre-visit readings very slowly. During the summer and with new electrodes, the pH readings typically returned to pre-visit levels within 1 hour. An old electrode or winter conditions often resulted in a recovery and flagging period of 6 to 8 hours. Flagging was terminated when the pH returned to within 0.05 unit from initial values, or when pH readings were stable for 1 hour.

If either pH or conductivity were determined to be out of calibration based on QC checks described previously, the data collected since the previous QC check for that probe were flagged. Although much of these data are likely to be valid, they all must be considered suspect as the initiation of invalid data cannot be pinpointed. The end user then is responsible for deciding if and how the flagged data are used.

Data Compilation and Summarization

Following validation and verification, all data were added to the master data file. Separate master files were developed for Minimonitor and streamflow data, and grab-sample, stormflow, lysimeter, precipitation, and throughfall chemistries and volumes.

Appropriate flags were included in the data files (Table 4). Minimonitor pH and conductivity data collected during and immediately following the application of the fertilizer (24 to 48 hours) were not included in the master data file; however, they were retained in separate files so that the information would remain available. Because of the size of the master data sets, data were stored on magnetic tapes; a hard copy was retained in a separate location. A second set of magnetic tapes also was kept at another location as a backup.

A report describing major activities and instrument or analytical problems was prepared at the end of each quarter. Results of the QA/QC checks were summarized, primarily in tabular form. These summaries included percent of conductivity and ion balance checks that failed, percent of failed QCCS and resulting number of reruns, number of holding-time violations, number of field blanks flagged for contamination, relative percent difference between duplicate samples, and an overall accuracy and precision summary for all quality-control check samples.

Percent quality assurance (QA) completeness also was calculated for each quarter using the conductivity and ion-balance check data:

$$\%\ \text{QA Complete} = \frac{\text{(Total No. of Samples Analyzed)} - \text{(No. of Samples Flagged for \% Ion Diff. or \% Cond. Diff.)}}{\text{Total No. of Samples Analyzed}} \times 100$$

A similar calculation of percent QC completeness was determined each quarter using QCCS and holding-time flag information:

$$\%\ \text{QC Complete} = \frac{\text{(Total No. of Individual Analyses)} - \text{(No. of Individual Analyses Flagged for QC Violations)}}{\text{Total No. of Analyses}} \times 100$$

Table 4.—Flags for chemistry and Minimonitor data files

Data file	Flag	Condition
Chemistry	F	Holding time exceeded
	D	QCCS outside of acceptable limits
	H	No QCCS included in batch
	I	Analysis not required
	G	Not enough sample, sample lost, or calculation not possible
	J	Ion balance and/or calculated conductivity check outside of acceptable limits
	K	Result given is the result from reanalysis
	A	Original result accepted after reanalysis
	Z	Result given is less than instrument detection limit
	R	Result is greater than instrument dynamic range, but is acceptable because analysis was done using dilution
Minimonitor	Q	QC or calibration visit
	D	QCCS outside of acceptable limits

Discussion

For this study, sample handling, processing, and analytical methods were changed significantly from our traditional procedures. Full implementation of the approved QA plan in the laboratory was not completed until June 1988. Consequently, the April-June 1988 quarter (Table 5), which actually included only May 1-June 30, had an extremely low percent QC completeness. The 80-percent QC completeness required by the EPA was met during all quarters except that quarter and the fourth quarter of 1991. QC completeness for the latter quarter fell below 80 percent because storm samples were collected during the Thanksgiving and Christmas holiday periods.

The large number of samples exceeding holding times for the first two quarters in 1989 was attributed partially to downtime of the DOC and ammonia analyzers and an extended illness of one of the analysts.

The EPA-required 80-percent QA completeness was exceeded during all quarters (Table 6). The number of samples that failed the ion balance check and/or conductivity check represent those samples that failed even after all reanalyses and retesting were completed. The lowest QA completeness was 95.18 percent.

The quarterly summary of accuracy and precision for quality-control check samples is given in Table 7. Alkalinity/acidity results are based only on the pH of the QCCS.

Percent accuracy was calculated as:

$$\%A = \frac{\text{Average Measured Value} - \text{Theoretical Value}}{\text{Theoretical Value}} \times 100$$

Percent precision was calculated as:

$$\%P = \frac{\text{Standard Deviation of Values}}{\text{Mean Measured Value}} \times 100$$

Most of the quality-control samples that did not meet EPA goals occurred during the first two quarters as the new procedures were being implemented. After the first two quarters of 1988, only sulfate QCCS precision during the first quarter in 1989 did not meet EPA goals. The worst results were for the April-June and July-September 1988 quarters. At that time we discovered that our sulfate standard was contaminated with chloride; standards procured from a new source eliminated this problem.

Table 5.—Quarterly quality control completeness summaries

Quarter	No. of analyses	Holding time exceeded	Samples affected by failed QCCS	Percent completeness
		Number		
April-June 1988	1275	283	405	46.04
July-Sept. 1988	1122	0	38	96.61
Oct.-Dec. 1988	1368	32	0	97.66
Jan.-March 1989	6466	610	45	89.87
April-June 1989	6092	715	60	87.67
July-Sept. 1989	2125	158	2	92.47
Oct.-Dec. 1989	3978	75	15	97.86
Jan.-March 1990	4624	214	0	95.37
April-June 1990	4526	156	0	96.55
July-Sept. 1990	3948	381	0	90.37
Oct.-Dec. 1990	4069	768	6	81.17
Jan.-March 1991	4885	254	42	94.80
April-June 1991	3010	447	7	85.15
July-Sept. 1991	1394	41	5	96.92
Oct.-Dec. 1991	1163	305	0	73.60

Table 6.—Quarterly quality assurance completeness summaries

Quarter	No. of samples	Samples failing ion balance check	Samples failing conductivity check	Percent completeness
		Number		
April-June 1988	117	0	0	100.00
July-Sept. 1988	104	1	3	95.18
Oct.-Dec. 1988	123	0	0	100.00
Jan.-March 1989	561	0	0	100.00
April-June 1989	528	3	3	98.47
July-Sept. 1989	195	0	2	97.37
Oct.-Dec. 1989	367	0	0	100.00
Jan.-March 1990	387	0	0	100.00
April-June 1990	384	0	0	100.00
July-Sept. 1990	337	0	0	100.00
Oct.-Dec. 1990	343	0	0	100.00
Jan.-March 1991	411	0	0	100.00
April-June 1991	256	1	0	99.45
July-Sept. 1991	117	0	0	100.00
Oct.-Dec. 1991	97	0	0	100.00

Duplicate results are presented in Table 8. Relative percent differences (RPD) between duplicates were calculated for each duplicate pair by:

$$RPD = \frac{|X_1 - X_2|}{\text{Mean } X} \times 100$$

and then averaged per quarter by analyte. A low RPD value indicates little variation within duplicates. Acceptable RPD values had to be less than the worst case control limits in Table 2.

The EPA's RPD goal for dissolved organic carbon (DOC) was not achieved for any quarter. In fact, except for October-December 1988, the percentage of pairs that met the RPD goal for DOC never exceeded 50. Because the QCCS precision (Table 7) for DOC was acceptable, part of the disparate results may be a reflection of the difficulty in obtaining true duplicates for DOC. Most of the duplicates were obtained from lysimeter samples which also have the most variable characteristics of all of the sample types collected. In addition, lysimeters have the greatest DOC concentrations of all sample types during most of the year. Aside from DOC, only the sodium results during April-September 1990 and chloride results during April-June 1990 were less than EPA goals (by less than 1 percent).

Results for field-blank contamination are given in Table 9. During July-December 1990, distilled water was taken from a contaminated reservoir. Once discovered, the contamination was eliminated. It is not known why so many field blanks were contaminated especially during the first 2 years; most of the contamination during this period was attributed to electrical conductivity and chloride. The electrical conductivity threshold was exceeded due to the presence of chloride. In most instances, the chloride contamination was only slightly greater than the limits allowed. Also, it was not considered a major concern because chloride in streams, soils, and precipitation in this area are of minor consequence.

Of the 1,751 groups of washed bottles tested for contamination before being used in the field, only 7 had electrical conductivities greater than 2 μS cm^{-1}. This number is only 0.4 percent of all groups of bottles tested; none failed the second test following rerinsing.

Field monitoring began before approved laboratory procedures were fully implemented. Minimonitor data were collected beginning about 4 months earlier on December 20, 1987. Completeness for each Minimonitor parameter (Table 10) was calculated by dividing the total number of data points minus the number of points flagged for failed QCCS results by the total number of data points. The results were multiplied by 100 to express each as a percent. No data points recorded during QC visits or during electrode or cell recoveries were used in this calculation.

Table 7.—Quarterly percent accuracy and percent precision summaries by analyte

	pH		Cond		Alkalinity and acidity		Cl		NO_3		SO_4		DOC		Ca		Mg		Na		K		NH_4	
Quarter	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P	%A	%P
April-June 1988	-0.25	1.09	-0.36	5.67	—	—	-20.00	6.26	-7.00	1.09	-3.38	0.89	—	—	-4.00	3.68	-1.00	1.81	4.50	1.28	-9.00	5.18	0.00	1.24
July-Sept. 1988	0.21	0.56	-1.73	4.82	0.16	0.77	0.10	7.10	-2.62	2.20	-1.03	1.58	—	—	2.99	1.85	3.48	2.09	3.60	6.13	-0.01	3.05	0.16	1.33
Oct.-Dec. 1988	-0.32	0.82	-2.08	3.20	0.02	0.92	1.42	4.38	-2.70	3.74	0.05	0.89	0.60	0.00	0.65	1.59	0.78	1.61	1.72	2.12	-0.05	1.39	-0.04	1.04
Jan.-March 1989	0.36	0.68	0.08	3.37	0.78	0.44	-0.76	3.32	-0.77	1.17	-1.34	6.88	0.06	3.38	1.93	2.08	-0.08	0.78	0.73	1.58	-2.27	2.04	1.06	2.07
April-June 1989	0.33	0.67	1.04	3.06	0.45	1.19	-2.47	3.59	-1.94	1.07	0.00	1.21	2.87	2.97	0.56	1.39	0.11	0.54	1.49	1.02	-0.25	1.45	-0.91	2.72
July-Sept. 1989	-0.12	0.55	1.30	2.86	0.67	0.64	-1.13	2.86	-1.49	1.46	-0.22	1.93	0.29	3.46	1.01	1.11	0.01	0.53	1.13	0.87	-0.39	1.60	-3.82	1.77
Oct.-Dec. 1989	0.03	0.63	0.55	2.82	0.48	1.06	-0.33	4.19	-1.11	1.16	-0.35	1.55	2.69	3.08	0.41	0.83	0.16	0.51	1.72	0.87	0.68	1.15	-0.50	2.35
Jan.-March 1990	0.78	0.64	3.68	2.93	0.51	0.88	3.14	2.94	-0.18	1.65	-0.60	1.61	2.74	2.79	-0.56	1.05	1.15	1.08	1.24	0.93	0.22	1.68	2.38	1.98
April-June 1990	-0.43	0.65	1.17	4.15	0.53	0.84	0.28	1.90	-0.41	0.81	-0.37	1.27	2.77	2.32	-0.09	1.00	0.63	0.51	1.27	1.03	-0.62	1.09	4.98	0.77
July-Sept. 1990	-0.18	0.70	0.59	2.35	0.11	0.81	0.45	1.75	-0.13	0.49	-0.42	0.76	4.35	3.80	-0.05	1.09	0.49	0.53	1.19	0.97	-0.28	1.32	3.73	1.33
Oct.-Dec. 1990	-0.05	0.59	0.55	2.88	-0.14	0.98	1.85	1.85	-2.03	3.29	-0.50	0.91	0.61	2.42	-0.64	1.04	0.42	0.54	0.25	0.80	-0.55	1.18	2.24	0.92
Jan.-March 1991	-0.06	0.56	0.96	2.16	-0.05	1.24	0.63	2.33	-1.11	2.41	-0.95	1.00	2.66	3.72	-0.22	0.82	0.11	0.61	1.28	0.91	-1.65	1.20	2.09	1.23
April-June 1991	-0.30	0.69	1.87	0.00	-0.26	0.91	1.65	2.04	-0.90	1.00	0.28	1.93	4.28	2.22	0.76	1.30	0.01	0.59	-0.10	1.04	-0.81	1.01	1.24	1.24
July-Sept. 1991	-0.12	0.39	2.01	2.41	0.36	0.86	-1.17	2.91	0.03	0.44	-1.66	1.94	5.47	3.30	0.03	1.04	-0.10	0.56	-0.55	1.12	-1.26	1.08	0.35	0.87
Oct.-Dec. 1991	-0.08	0.52	-0.25	3.12	-0.49	1.02	3.07	2.60	0.00	0.83	-0.25	1.17	0.03	0.00	-0.21	0.72	0.14	0.58	0.02	0.71	-1.00	1.07	0.55	1.04

Table 8.—Quarterly summaries of relative percent differences (RPD) for duplicates and percent of analyses passing the RPD test criteria

	pH		Conductivity		Cl		NO_3		SO_4		DOC		Ca		Mg		Na		K		NH_4	
Quarter	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass	RPD	%Pass
Oct.-Dec. 1988	—	—	—	—	2.95	78.6	0.61	100.0	0.77	100.0	8.48	66.7	1.01	100.0	1.55	100.0	2.31	92.3	1.36	100.0	0.00	100.0
Jan.-March 1989	0.56	100.0	3.68	77.3	2.17	95.5	1.29	95.2	0 18	100.0	12.46	50.0	1.74	95.2	0.90	95.5	2.67	72.7	1.35	95.5	0.81	94.7
April-June 1989	0.49	95 8	3.18	83.3	3.98	70.8	1.70	91.3	0.70	100.0	12.71	47.8	2.54	86.4	0.76	100.0	3.12	70.8	3.99	66.7	0.00	100.0
July-Sept. 1989	0.68	100.0	2.40	100.0	0.87	100.0	0.49	100.0	0.67	100.0	16.59	50.0	0.53	100.0	0.00	100.0	0.38	100.0	1.46	100.0	0.00	100.0
Oct.-Dec. 1989	0.25	100.0	2.61	83.3	2.36	100.0	0.71	100.0	0.64	100.0	18.31	16.7	0.57	100.0	0.51	100.0	1.86	100.0	0.95	100.0	0.00	100.0
Jan.-March 1990	0.32	100.0	3.13	87.5	4.02	92.0	2.24	95.8	0.81	100.0	16.26	44.0	1.49	92.0	1.16	92.0	2.01	76.0	1.61	92.0	0.50	95.2
April-June 1990	0.32	100.0	2.25	86.4	5.54	81.8	2.27	100.0	2.20	95.5	22.79	22.7	1.90	90.9	2.15	90.9	5.84	45.5	2.26	86.4	0.86	100.0
July-Sept. 1990	0.62	100.0	2.67	83.3	3.50	100.0	1.98	100.0	1.56	100.0	26.65	16.7	1.72	83.3	2.08	83.3	5.17	50.0	2.40	66.7	0.00	100.0
Oct.-Dec. 1990	0.51	100.0	0.94	100.0	0.50	100.0	0.38	100.0	0.53	100.0	10.63	33.3	1.08	100.0	1.10	100.0	2.45	83.3	0.92	100.0	0.00	100.0
Jan.-March 1991	0.90	95.5	2.61	90.9	19.85	50.0	4.57	85.7	1.66	90.9	13 83	42.1	1.85	85.7	1.59	90.9	2.51	81.8	2.14	95 5	0.28	100.0

Table 9.—Quarterly field blank contamination summaries

Quarter	Number of field blanks	Contaminated samples	
		Number	Percent
April-June 1988	14	5	35.7
July-Sept. 1988	12	6	50.0
Oct.-Dec. 1988	20	8	40.0
Jan.-March 1989	35	10	28.6
April-June 1989	36	16	44.4
July-Sept. 1989	20	1	5.0
Oct.-Dec. 1989	30	4	13.3
Jan.-March 1990	31	5	16.1
April-June 1990	32	10	31.3
July-Sept. 1990	28	14[a]	50.0
Oct.-Dec. 1990	33	9[b]	27.3
Jan.-March 1991	32	5	15.6
April-June 1991	23	0	0.0
July-Sept. 1991	16	2	12.5
Oct.-Dec. 1991	8	0	0.0

[a]4 blanks from same source.
[b]5 blanks from same source.

Table 10.—Quarterly summaries of Minimonitor completeness by parameter and for all parameters combined

Quarter	Completeness			
	Temperature	Conductivity	pH	Total
	Percent			
Jan.-March 1988	99.82	91.11	82.98	88.42
April-June 1988	100.00	50.97	77.55	76.17
July-Sept. 1988	100.00	92.81	62.57	85.13
Oct.-Dec. 1988	100.00	90.28	96.34	95.54
Jan.-March 1989	100.00	93.78	77.26	90.35
April-June 1989	100.00	80.09	93.56	91.22
July-Sept. 1989	100.00	96.47	81.76	92.74
Oct.-Dec. 1989	100.00	93.77	86.69	93.49
Jan.-March 1990	100.00	100.00	91.87	97.29
April-June 1990	100.00	68.58	80.21	82.93
July-Sept. 1990	100.00	95.93	92.25	96.06
Oct.-Dec. 1990	100.00	100.00	69.96	89.99
Jan.-March 1991	100.00	96.78	64.20	86.99
April-May 1991	100.00	92.31	76.48	89.60
July-Sept. 1991	100.00	95.17	90.58	95.25
Oct.-Dec. 1991	100.00	97.87	96.30	98.06

Conductivity completeness was low during the first spring (second quarter 1988) that the Minimonitors were operated. Most of the flagged data were recorded during the period of rapid changes in stream temperature and before we realized how quickly and dramatically the temperature changes affected conductivity

Percent pH completeness was low in the second and third quarters of 1988. During this period we were developing protocols for determining when it was necessary to recalibrate or replace electrodes. As the details were worked out, completeness rose.

Percent completeness for pH dropped again from October 1990 to May 1991. Problems arose with the performance of field and backup electrodes, and efforts to rejuvenate them were unsuccessful. Percent completeness was low until these electrodes were replaced. Once new electrodes were in place, completeness returned to levels exceeding 90 percent.

Overall, pH measurements were the most difficult of the three parameters to maintain at an acceptable level. In most quarters we were able to keep completeness above 80 percent after altering some of the initial protocols and gaining experience with the Minimonitors

Conclusion

We believe the data obtained from this study are of a high quality as a result of implementing and following approved QA/QC protocols. Frequently when QA/QC results fell below desired levels, it was possible to trace the source of the problem to a protocol not being followed.

All field and laboratory protocols were flexible so that changes could be made if a protocol was deemed unreasonable, insufficient, or unattainable. Flexibility was particularly necessary in the field, where working conditions often were less than desirable.

We strongly recommend that all research studies begin only after procedures for quality control and quality assurance have been considered thoroughly and documented in the study plan. It is useful to test previously unimplemented protocols and procedures to identify potential problems before a study is begun and data are jeopardized. The investment in time and effort to develop solid QA/QC procedures will be recouped many times over in the compilation of accurate data.

Acknowledgments

Sincere thanks is extended to the Watershed Management Project field and laboratory staff of the Timber and Watershed Laboratory for their patience, cooperation and flexibility while these QA/QC procedures were being developed and implemented. We also appreciate the contributions made by Linda Loughry who typed and formatted this manuscript This manuscript has not been subjected to review by the EPA and, therefore, does not necessarily reflect the views of that Agency and no official endorsement should be inferred.

Literature Cited

Bigelow, David S.; Dossett, Scotty R. 1988 **Instructions manual NADP/NTN site operation: National Atmospheric Deposition Program.** Fort Collins, CO: Colorado State University, Natural Resource Ecology Laboratory.

Edwards, P. J.; Wood, F. 1992. **The effects of watershed acidification on soil water and stream water chemistry.** In: Proceedings, 1992 spring meeting of the American Geophysical Union, Canadian Geophysical Union, and Mineralogical Society of America; 1992 May 12-16; Montreal, PQ. Washington, DC: American Geophysical Union: 121. Abstract.

Kochenderfer, James N.; Edwards, Pamela J. 1990. **Design and construction of a low-cost stream-monitoring shelter.** Gen Tech. Rep. NE-135 Broomall, PA: U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station.

Peden, M. E. 1981. **Sampling, analytical, and quality assurance protocols for the National Atmospheric Deposition Program.** ASTM D-22 symposium and workshop on sampling and analysis of rain. Philadelphia, PA: American Society for Testing and Materials.

Strickland, T. C.; Wildensee, F. 1990. **Sulfur and nitrogen cycling in soils of two watersheds in the Fernow Experimental Forest in the central Appalachian mountains.** In: Proceedings, 1990 annual meetings of American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America; 1990 October 21-26, San Antonio, TX. Madison, WI: American Society of Agronomy: 340 Abstract

U.S. Environmental Protection Agency 1987. **Handbook of methods for acid deposition studies: laboratory analysis for surface water chemistry.** Washington, DC: U.S. Environmental Protection Agency.

Weast, Robert C., ed. 1988. **CRC handbook of chemistry and physics.** 68th ed. Boca Raton, FL: CRC Press.

Wildensee F.; Strickland, T. C 1990. **Nitrogen processing in soils of two watersheds in the Fernow Experimental Forest in the central Appalachian mountains.** In: Proceedings, 1990 annual meetings of American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America; 1990 October 21-26; San Antonio, TX. Madison, WI: American Society of Agronomy: 341 Abstract