

QUALITY ASSURANCE REPORT
LOCH VALE WATERSHED PROJECT

SURFACE WATER CHEMISTRY
1983 - 1987

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ABBREVIATIONS USED IN THIS REPORT

QA	Quality Assurance
QC	Quality Control
DQO	Data Quality Objective
NPS	National Park Service
USGS	United States Geological Survey
NADP	National Atmospheric Deposition Program
EPA	Environmental Protection Agency
NBS	National Bureau of Standards
CSU	Colorado State University
NREL	Natural Resource Ecology Laboratory
PVC	Polyvinyl Chloride
PC	Polycarbonate
LIS	Low Ionic Strength
DI	Deionized water
DOC	Dissolved Organic Carbon
ANC	Acid Neutralizing Capacity
AAS	Atomic Absorption Spectrophotometry
ICP	Inductively Coupled Plasma Spectrophotometry
DCP	Direct Current Plasma Spectrophotometry
IC	Ion Chromatography
AWC	Automated Wet Chemistry

All elements, compounds, and ions are referred to by their chemical symbols. Standard postal abbreviations are used for names of states.

1. INTRODUCTION:

In 1980, the National Park Service initiated research in Loch Vale Watershed of Rocky Mountain National Park funded by the Aquatic Effects Research Program of the National Acid Precipitation Assessment Program. Major goals of the project are twofold: 1.) Understanding processes within the watershed which interact with water from precipitation to mitigate or accelerate the effects of anthropogenic inputs, and 2.) Long term ecological monitoring of the watershed.

The research aspect of the project involves synthesis of many types of data of varying degrees of numerical precision. Some of these data involve qualitative observations to which firm estimates of precision cannot be assigned. In these cases it is impossible to quantify the uncertainty of calculated values. Innovative approaches must be used to evaluate the quality of such data. These data may be used in various ways by different studies within the project, and each of these studies must address the issue of uncertainty in measured and calculated values as used in that study. This report, therefore, makes no attempt to evaluate the quality of these types of data.

Long term ecological monitoring of the watershed requires the collection of information of several types. These include data such as soil maps and vegetation inventories which are collected once or very infrequently. Any uses of these data are subject to the cautions listed above, and such uses must be accompanied by careful evaluations of data quality in the context of the specific study. Another important component of the monitoring aspect of the project is the collection of chemical data on the composition of water in precipitation, lakes, and streams. These data characterize the current status of water quality in the watershed and may be used at a later date to detect trends in the parameters measured. Estimates of uncertainty of these chemical data are needed so that comparisons can be made at the appropriate level of precision, and to assist in the evaluation of the quality of calculated values based on these measurements.

Routine sampling began in Loch Vale in 1982, and the NADP site was established in the watershed in October, 1983. Lake and stream samples were analyzed by the University of Montana Biological Station until 1982. Since that time all surface water samples have been analyzed at the USGS National Water Quality Laboratory (herein referred to as the USGS Lab) in Arvada, CO. All samples of precipitation are analyzed by the Central Analytical Laboratory of the Illinois State Water Survey in Champaign, IL. The QA/QC procedures of the

NADP network are well documented [1,6]. This report documents the quality of chemical data provided by the USGS Lab. Data generated by the University of Montana are not evaluated, but will be in a later report.

This report details QC procedures used by the project to minimize errors in the estimates of chemical composition of surface water samples. Data quality is then evaluated using field blanks, co-located samples, ion balance calculations, and comparisons of theoretical conductance to measured values. Finally, planned improvements in QA/QC for the future are discussed.

2. QUALITY CONTROL:

This section addresses procedures used to minimize uncertainty introduced in each component of the measuring process identified above.

2.1. QC Activities in the Field

Surface water samples are collected by established sampling protocols which are written and strictly adhered to. All sampling containers are acid-washed in 10% HCl at least 6 hours and then rinsed at least five times with deionized water (DI) and stored wet with DI. The DI typically has conductance under $1.0 \mu\text{S}/\text{cm}$. Before use, DI stored in the containers is measured for specific conductance. Any bottle with conductance greater than $2.0 \mu\text{S}/\text{cm}$ is rejected and re-cleaned. Typical values for the stored DI range from 0.6 to $1.2 \mu\text{S}/\text{cm}$. Before sampling, the bottles are rinsed three times with the solution to be collected, including the cap and threads of the bottle.

Stream samples from the Loch Outlet, the only outlet to the watershed, are collected weekly from May through December. Daily outlet samples are collected during the early stage of the spring snowmelt. Other stream reaches are sampled monthly during the summer (June through September). Stream samples are collected by simply dipping the bottle in the stream by hand. Rubber gloves are used for this procedure, and care is taken to hold the sampling bottle upstream of the hand.

Lakes are sampled monthly during the summer and semi-monthly during the rest of the year. Lake samples are taken by peristaltic pump from a boat in the summer and through a hole chopped in the ice during the winter. The tubing in the pump through which the sample passes is periodically replaced. The tubing is acid-washed between sampling cycles, and rinsed thoroughly with DI following each use. Before collecting any sample, the pump is flushed thoroughly with the water to be collected. Lakes are sampled from the surface down to avoid suspending bottom sediments in the water column.

Snow cores are collected at one site in the watershed on a monthly basis during the winter and early spring. Cores are collected in an acid-washed, DI-rinsed PVC tube which is pushed down to the plastic sheet placed on top of the snow after the previous month's collection. The snow is then placed in a DI-rinsed polypropylene bag (BelArt Products). The sample is double-bagged to prevent leakage or contamination. Snow samples are allowed to melt at room temperature, usually overnight. As with other samples, the core tube is rinsed with the

snow three times before the sample is collected.

2.2. QC in the Field Laboratory

Surface water samples are processed upon arrival at the field laboratory in the park. Time elapsed between collection and processing ranges from one to four hours.

Since July 20 1987, separate subsamples of lake and stream water to be used for pH and conductance measurements have been collected in Luer-Lock syringes to avoid equilibration of the sample with atmospheric CO₂. These samples are then analyzed for pH using a closed cell sample chamber of a design similar to that of the National Surface Water Survey [5]. All pH's are measured on an Altex 3500 meter with Beckman combination electrodes (model 39835). The meter is calibrated with NBS traceable buffers at pH 4.0 and 7.0, and checked with dilute HNO₃ at pH 4.30, which approximates the ionic strength of the samples being analyzed (specific conductance about 22 μS/cm). The electrode is allowed to equilibrate in an aliquot of each solution being measured (including buffers and QC check solution), then a fresh aliquot is used for the final reading. The check solution is analyzed before any water sample and after each 5 samples. If the measured pH of the check solution is outside the range 4.30 +/- 0.1, the meter is recalibrated and all samples run since the last check sample reading are reanalyzed, providing enough sample remains for this purpose. All pH measurements, analytical parameters, check solution pH's, and electrode performance notes or maintenance procedures are recorded in a pH journal and archived for future reference.

Since June 1987, samples for DOC analysis have been collected in glass bottles with aluminum foil lid seals. The bottles and foil are baked in a muffle furnace at 500 C for five hours prior to use. The DOC samples are filtered in the field lab through baked glass fiber or silver filters using baked filtration apparatus, and the sample shipped in another baked glass bottle.

All other sample filtrations are performed using an Antlia peristaltic filter pump. Tubing in the pump is replaced periodically, flushed thoroughly with DI water between samples, and flushed with sample before the filtered subsample is collected. Filters used are Nucleopore 0.4 μm PC membrane filters 45 mm in diameter. Containers for filtered aliquots are rinsed three times with filtered sample, including caps and threads.

Sample preservation for cation and metals analysis is accomplished by addition of 1 ml of reagent grade, quality controlled HNO_3 supplied in ampoules by the USGS. Aliquots to be used for nutrient analysis (NH_4 , PO_4) are preserved with reagent grade HgCl_2 supplied in similar ampoules from the USGS lab. These aliquots are placed in opaque bottles and kept refrigerated at the USGS lab prior to analysis. This preservation technique was found to be superior to the use of chloroform, sulfuric acid, or simple refrigeration in a study conducted at the USGS lab [3]. These ampoules of sample preservative have been available since 1986. Prior to that time, USGS provided us with mercuric chloride tablets as a biopreservative.

All samples are kept refrigerated in the dark until shipment to the USGS. Samples are shipped packed in ice in coolers within 24 hours of collection. If sample collection is late in the week and there is a possibility of the cooler being left unrefrigerated in the mail over the weekend, the samples are shipped by Express Mail or Federal Express to insure they arrive and are processed before the weekend.

2.3. QC Activities at the USGS Laboratory

Analytical methods used by the USGS Laboratory are detailed in [2]. QA/QC practices are well documented and published elsewhere [4]. In 1985, the laboratory created a separate section for the analysis of low ionic strength (LIS) samples. Analytical methods are the same as for other samples, but instruments are dedicated to dilute waters to avoid contamination, facilitate calibration, and increase sensitivity. The criterion for samples to be analyzed in the LIS section is a specific conductance of less than $300 \mu\text{S}/\text{cm}$. All samples submitted for analysis by the Loch Vale Watershed project have been analyzed by this section since its creation.

3. QUALITY ASSURANCE:

Table 1 lists the parameters recorded for each sample analyzed by the USGS Laboratory. The number of values recorded for each sample varies because all parameters are not determined for every sample, and because this total does not include outliers, defined as values lying more than four standard deviations from the mean concentration for that analyte [9].

TABLE 1 PARAMETERS RECORDED FOR SURFACE WATER SAMPLES			
ANALYTE	REPORTING UNITS	NUMBER OF VALUES	ANALYTICAL METHOD(S)
Field pH	pH	1030	pH electrode
Lab pH	pH	711	pH electrode
Field Cond	$\mu\text{S}/\text{cm}$	1045	conductance cell
Lab Cond	$\mu\text{S}/\text{cm}$	988	conductance cell
ANC	$\mu\text{eq}/\text{l}$	792	Titration
Ca	mg/l	982	AAS & ICP
Mg	mg/l	981	AAS & ICP
Na	mg/l	985	AAS & ICP
K	mg/l	980	AAS
NH_4	mg/l	973	AWC
SO_4	mg/l	980	IC
NO_3	mg/l	1020	IC
NO_2	mg/l	538	AWC
PO_4	mg/l	963	IC & AWC
Cl	mg/l	977	IC
F	mg/l	984	IC
Br	mg/l	980	IC
SiO_2	mg/l	976	ICP
Al	$\mu\text{g}/\text{l}$	684	DCP
Fe	$\mu\text{g}/\text{l}$	1035	ICP
Mn	$\mu\text{g}/\text{l}$	968	ICP
DOC	mg/l	237	Wet Oxidation
Color	Pt-Co	415	Platinum-Cobalt
Acidity	mg/l as H	631	Titration

3.1. Bias in the Data

Sources of bias may include contamination in the handling or processing of samples, poor field measurements of pH and specific conductance, analytical bias at the USGS lab, and problems with data management. Laboratory bias is evaluated by external audit programs and the analysis of standard reference

materials. Sample contamination is best detected by analyzing field blanks. Bias introduced in data management is often difficult to detect, but evaluation of procedures will identify gross problems.

3.1.1. Laboratory Audits

Internal QA evaluations at the USGS include frequent analyses of blind audit samples, and daily analyses of standard reference materials [2,4]. External audits include one conducted by the EPA in 1986.

The only measurements made at the field laboratory are pH and specific conductance. The quality of these measurements is evaluated by external audits performed by the USGS for the NADP network. Artificial samples of precipitation are analyzed by project personnel, and by many other NADP sites. Table 2 compares measurements made at the NPS field laboratory with NADP values.

REPORT DATE	MEASURED pH	MEASURED COND.	NADP pH	NADP COND.
March 5, 1985	4.55	12.0	4.56	11.2
December 11, 1985	4.60	9.6	4.61	9.60
March 3, 1986	4.60	9.8	4.60	10.26
May 30, 1986	4.95	3.3	4.96	4.40
July 7, 1986	4.53	13.0	4.48	13.89
August 25, 1986	3.95	52.6	3.92	51.39
December 3, 1986	4.32	19.7	4.32	20.48
October 23, 1987	4.72	7.1	4.73	7.40
April 20, 1988	4.43	16.0	4.40	16.9

The NADP pH and conductance reported are the network averages for all sites participating in the comparison. For comparison studies reported through March, 1986, these are mean values. Starting with the comparison reported May 30, 1986, NADP reported median pH and conductance rather than mean, to avoid overemphasis on extreme values.

3.1.2. Collection and Analysis of Field Blanks

Field blanks consist of deionized water collected in the same container and by the same method as the corresponding normal sample. Storage time (if any) is also the same for blanks as for regular samples. Thus, if a snow sample is to be left overnight in a polypropylene bag to melt, the blank sample is also left in a

bag overnight. Results of analysis of three types of field blanks are presented in Table 3.

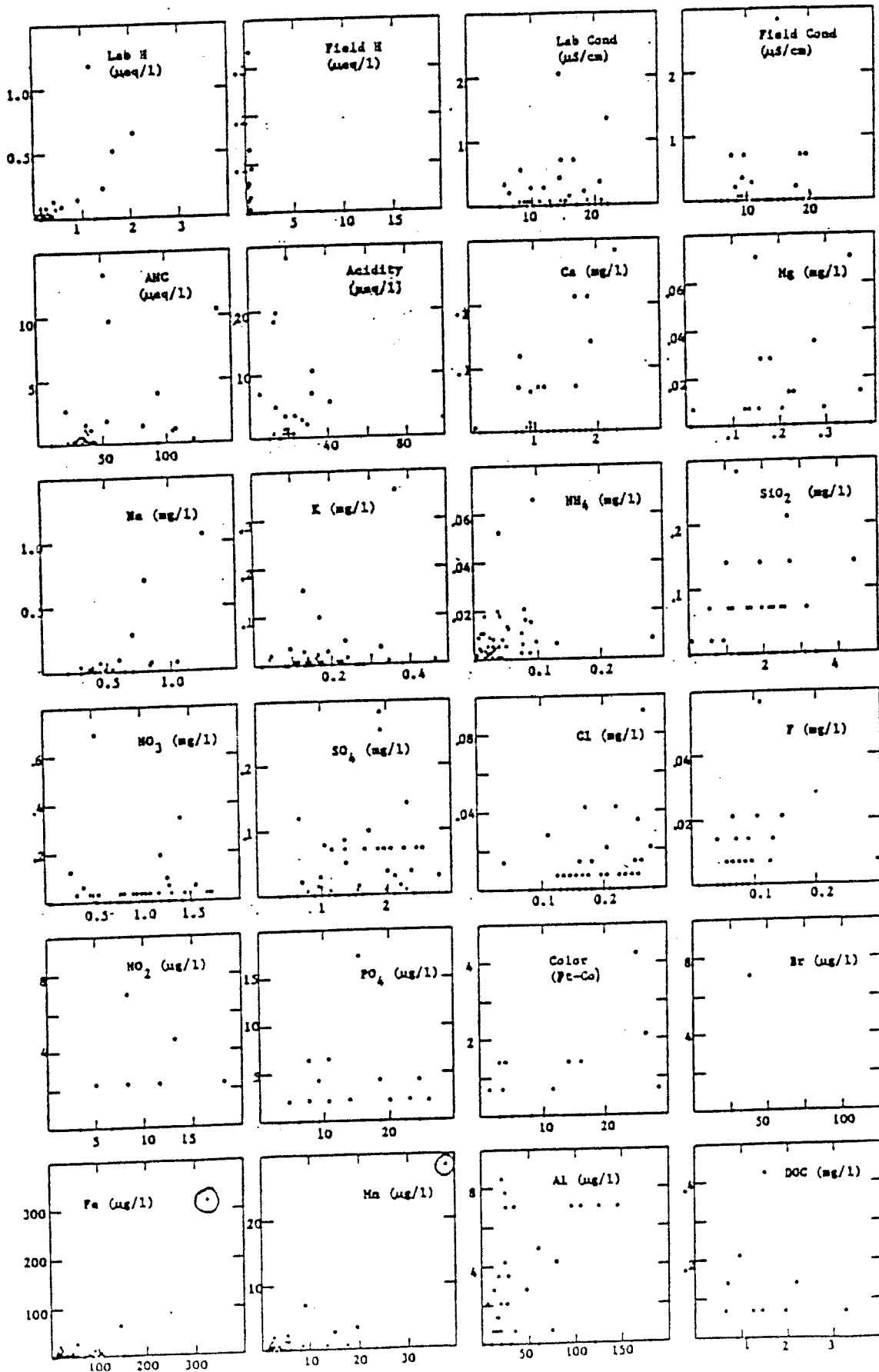
TABLE 3 BLANKS BY SAMPLE TYPE										
ANALYTE	UNITS	STREAM BLANKS			SNOW BLANKS			LAKE BLANKS		
		Mean Conc	Std Dev	N	Mean Conc	Std Dev	N	Mean Conc	Std Dev	N
Field pH	pH	6.15	0.65	6	-	-	0	5.50	-	1
Lab pH	pH	7.21	0.67	10	7.23	0.19	4	6.37	0.50	4
Field Cond	μS/cm	2.24	4.31	6	-	-	0	0.95	0.07	2
Lab Cond	μS/cm	4.36	4.70	11	2.75	2.87	4	0.98	0.05	5
ANC	μeq/l	-	-	0	-	-	0	5.0	7.0	2
Ca	mg/l	.135	.386	11	0.02	0	4	.014	.009	5
Mg	mg/l	.029	.029	10	0.01	0	4	.022	.018	5
Na	mg/l	.218	.060	11	0.20	0	4	.162	.085	5
K	mg/l	.010	.048	11	0.01	0	4	.016	.011	5
NH ₄	mg/l	.023	.028	11	.007	.003	4	.100	.133	5
SO ₄	mg/l	.020	.025	11	.015	.006	4	.025	.020	5
NO ₃	mg/l	.040	.013	11	.044	0	4	.036	.018	5
NO ₂	mg/l	.008	.007	0	-	-	0	.003	0	2
PO ₄	mg/l	.006	.007	10	.006	0	4	.010	.007	5
Cl	mg/l	.021	.021	11	0.01	0	4	.024	.031	5
F	mg/l	.019	.018	11	0.01	0	4	.018	.011	5
Br	mg/l	.031	.022	11	0.01	0	4	.008	.004	5
SiO ₂	mg/l	.186	.503	11	0.01	0	4	0.63	1.33	5
Al	μg/l	12.0	8.4	5	12.5	5.0	4	11.0	6.6	4
Fe	μg/l	4.82	4.36	11	3.25	0.50	4	15.8	13.6	4
Mn	μg/l	1.06	0.18	11	1.0	0	4	1.24	0.36	5
DOC	mg/l	0.20	-	1	-	-	0	0.30	-	1
Color	Pt-Co	2.0	2.0	4	1.5	0.6	4	0.5	0.7	2
Acidity	mg/l as H	.086	.036	6	-	-	0	.014	-	1

3.2. Precision of the Data

3.2.1. Collection of Co-located Samples

Precision of the measured values is estimated by the collection and analysis of co-located samples, or field duplicates. These are pairs of samples taken by identical methods at the same sampling location, as close together in time as possible. Actual elapsed time between samples in a duplicate pair is less than five minutes.

FIGURE 1
PRECISION PLOTS FOR DUPLICATE SAMPLES (1983 - 1987)
Standard Deviation vs. Mean Concentration



3.2.2. Calculation of Estimates of Data Precision

Precision is best reported as standard deviation [10]. Since precision often varies with concentration, plots of standard deviation against the mean concentration of the pair are preferable to pooled estimates of standard deviation from many pairs [7]. Such plots are presented for each analyte in Figure 1. In most cases, these plots show no relationship between standard deviation and concentration, so no attempt has been made to fit a curve to these data.

If the various pairs of duplicate samples are similar in concentration and precision, then the standard deviation of the entire set of measurements is estimated [9] by the formula

$$s = \sqrt{\frac{\sum d^2}{2k}}$$

where k is the number of pairs of duplicates and d is the difference in concentration of the given analyte between the individual measurements.

Inspection of the plots in Figure 1 reveals that the above conditions are met for most analytes. Precision plots for Fe and Mn, however, contain single points of very high concentration and standard deviation (circled in the figure) which should not be included in a pooled estimate of standard deviation by the above formula. These points were dropped from the data set and the above calculation was performed for each analyte. The results are reported in Table 4.

3.3. Other Measures of Data Quality

3.3.1. Charge Balance Calculations

Since all samples are electrically neutral, the sum of the measured cations should equal the sum of the measured anions. This principle is represented by a calculated parameter called the Ion Percent Difference (I%D), which is calculated as

$$I\%D = \frac{100 (\sum cations - \sum anions)}{\sum (cations + anions)}$$

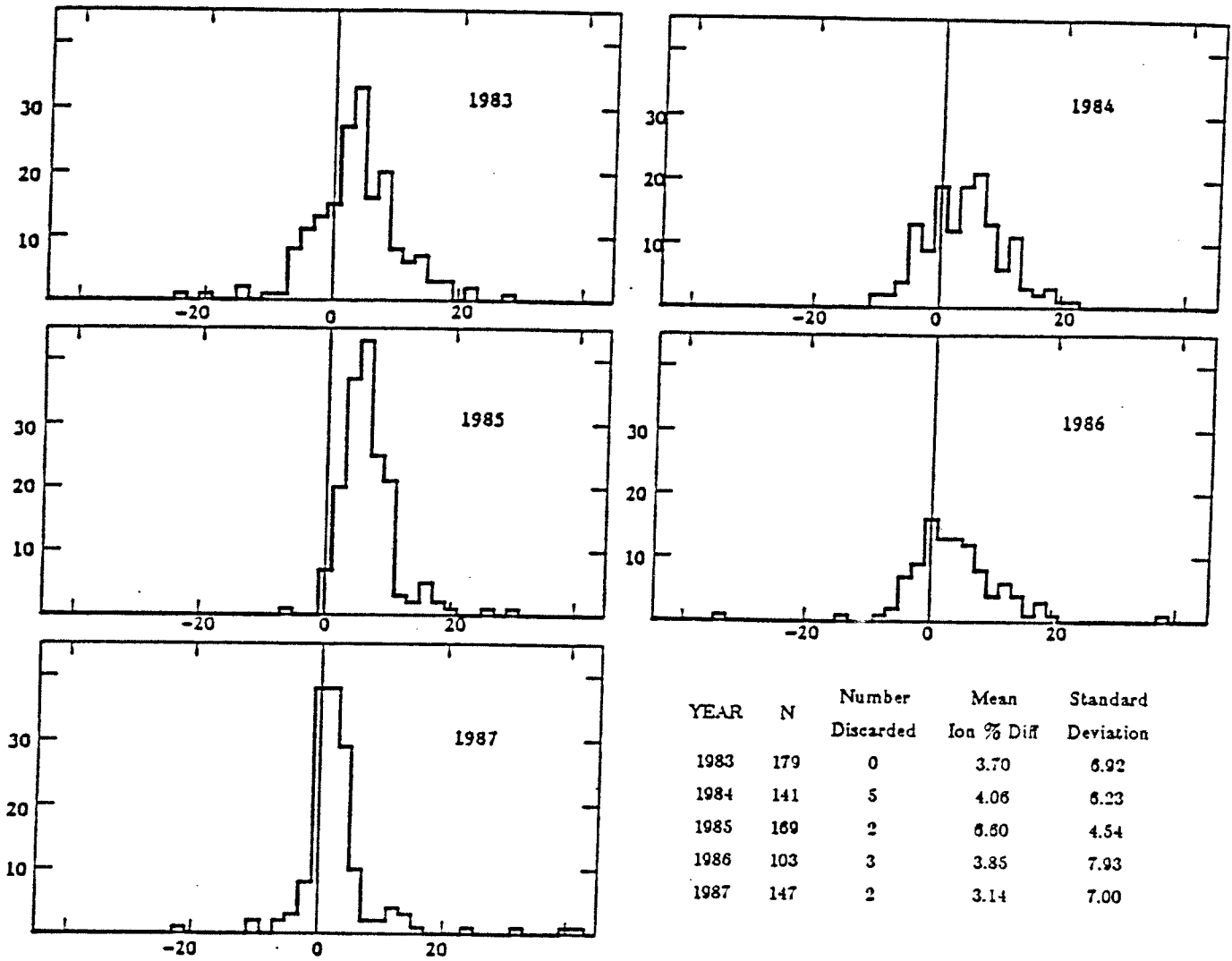
where all concentrations are expressed in microequivalents per liter. A negative value for I%D indicates an excess of negative charges whereas a positive I%D indicates an excess of positive charges. This calculation was performed for all samples, and the results are reported for each year in Figure 2.

TABLE 4
ESTIMATES OF PRECISION BY ANALYTE

ANALYTE	MEAN CONCENTRATION	STANDARD DEVIATION	RSD (PERCENT)	NUMBER OF PAIRS
Field Cond	12.515	0.450	3.59	51
Lab Cond	13.590	0.424	3.12	47
Field H	1.097	0.055	5.00	51
Lab H	0.534	0.257	48.15	34
ANC	52.706	4.060	7.70	31
Ca	1.365	0.070	5.11	48
Mg	0.215	0.020	9.40	48
Na	0.524	0.191	36.42	48
K	0.189	0.060	31.44	49
NH ₄	0.043	0.015	34.49	48
SO ₄	1.565	0.074	4.71	49
NO ₃	0.949	0.152	16.05	50
NO ₂	0.007	0.002	28.77	31
PO ₄	0.009	0.003	37.30	45
Cl	0.188	0.020	10.61	49
F	0.0840	0.011	13.44	48
Br	0.017	0.001	8.33	49
SiO ₂	1.808	0.078	4.31	48
Al	47.425	4.059	8.56	40
Fe	47.438	12.058	25.42	48
Mn	4.181	1.470	35.17	47
DOC	1.415	0.152	10.73	13
Color	9.500	1.208	12.71	24
Acidity	0.034	0.008	24.41	33

Samples for which all ions were not determined are not included in the charge balance calculations. Initial calculations yielded several samples which could not be included in Figure 2 at the present scale. Examination of the data for each of these samples showed that the calculated I%D is the result of obvious recording or transmission errors in the database. In several of these cases, for example, the concentration of a particular analyte was several orders of magnitude higher than reported for any other sample in the database. These samples were not included in the summary statistics presented in Figure 2.

FIGURE 2
FREQUENCY DISTRIBUTIONS OF CHARGE BALANCE
Ion Percent Difference (I%D)



3.3.2. Calculation of Theoretical Conductance

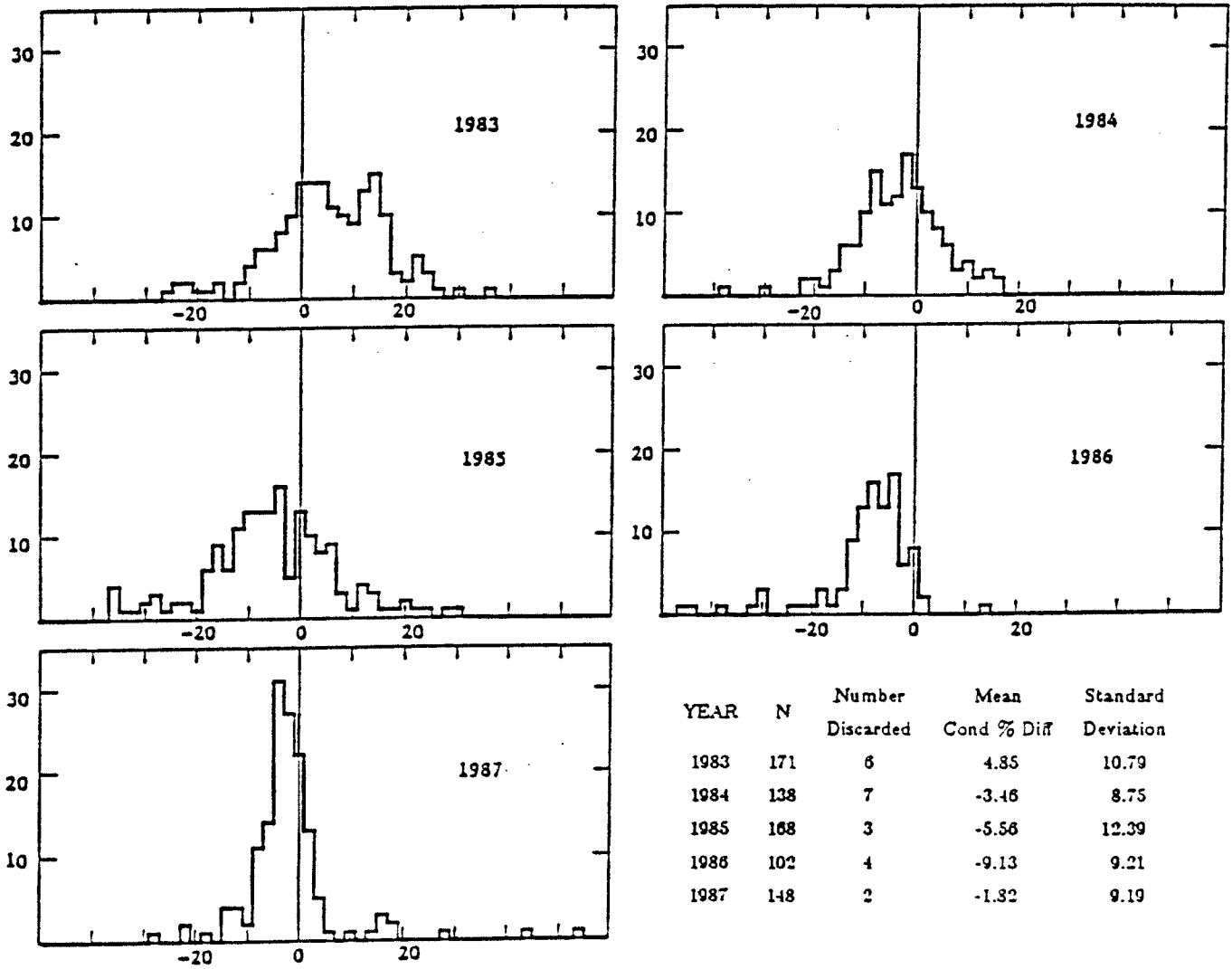
The theoretical conductance of a water sample may be calculated [8] by the formula

$$\begin{aligned} & [(H)(350) + (ANC)(43.6) + (Ca)(52.0) + (Cl)(75.9) + (Mg)(46.6) + \\ & (K)(72.0) + (Na)(48.9) + (NO_3)(71.0) + (SO_4)(73.9) + (NH_4)(74.5)] / 1000. \end{aligned}$$

where all concentrations are expressed in microequivalents per liter. This calculation was performed for all samples in the database, and the result compared to the specific conductance measured in the field laboratory. Since ANC is measured at the USGS Lab, the laboratory pH and conductivity are preferred over field values in this calculation, but since laboratory pH is often not recorded, field pH was used instead. Thus field conductance measurements were chosen for comparison. Conductance percent difference (C%D) was calculated for each sample as a percentage of the measured conductance. Positive values for C%D indicate that calculated conductance exceeds that measured in the field lab, and can indicate the presence of an overmeasured ion of either charge. Negative values can indicate an unmeasured or undermeasured species. Any deviation from zero, however, can also be the result of poor measurement of specific conductance. The frequency distribution of this parameter for each year is presented in Figure 3.

As was true for the plots of I%D, several samples for each year could not be included in the plots of C%D due to extreme values which lie outside of the presented scale. Sample by sample evaluation of the data showed that most of these samples were the same ones which have severe charge imbalances. Other outliers appear to be the result of poor conductance measurements as evidenced by large differences between field and laboratory values. Plots were constructed without the apparent outlier samples.

FIGURE 3
FREQUENCY DISTRIBUTIONS OF THEORETICAL CONDUCTANCE
Conductance Percent Difference (C%D)



4. DISCUSSION

4.1. Bias

The QA/QC procedures at the USGS Lab are adequate to detect and prevent the introduction of significant bias to the data. Field measurements of pH and specific conductance compare very well with those at other NADP sites as indicated by the Intersite Comparisons. The NADP 'acceptance window' is 0.1 units for pH and 4.0 $\mu\text{S}/\text{cm}$ for conductance. The field measurements made by this project have always fallen well within this criterion.

Analyses of field blanks show surprisingly high concentrations for many analytes. Much of the reason for this is that detection limit values are not currently flagged in the database. This also accounts for the frequent values of zero standard deviation among blank concentrations. This occurs whenever all blanks record the same detection limit value for an analyte. Detection limits vary from run to run, so this is not a reliable way to screen for such values.

The blank analyses look much better taking the detection limit values into account, but some concentrations are too high to be detection limits. These include Ca, Na, and SiO_2 in the stream blanks and Na, NH_4 , and SiO_2 in the lake blanks. The very high standard deviations in most of these cases indicate that most of this problem is due to one or two samples of high concentration unduly influencing the mean. Since only eleven stream blanks and five lake blanks have been analyzed, however, this problem must be studied further.

Snow blanks are less concentrated in most ions than either the lake or the stream blanks. This difference suggests a problem with sample handling and processing techniques for the lake and stream samples. Lake and stream samples are collected in bottles and filtered through a peristaltic filter pump not used in processing snow samples. These procedures will be examined in detail to determine if they introduce contamination to the samples.

4.2. Precision

The estimates of precision presented in Table 4 are conservative. Examination of the precision plots in Figure 1 indicates that many of the estimates are strongly influenced by one or two pairs of measurements with much higher standard deviation than the rest. Only for the cases of Fe and Mn was this difference so extreme as to require excluding the outliers from the calculation of the pooled uncertainty estimates, so the other estimates include such points. These analytes

include lab H, field H, field conductance, ANC, acidity, Mg, Na, K, NO₃, SO₄, Cl, F, PO₄, color, and DOC.

As expected, the major constituents of the water are estimated more precisely than those analytes present in less amounts. Exceptions to this pattern are partly due to the absence of detection limit flags noted above. The peculiar plot for Br in Figure 1, for example, includes 49 sample pairs, but since Br is rarely present in sufficient quantities to detect, only two sample pairs showed any difference at all, and exactly the same two concentrations are recorded for those pairs.

4.3. Charge Balance and Conductance Calculations

Distributions of the I%D for all of the years are nearly normal, as shown in Figure 2. The mean I%D is always positive, however, indicating an excess of positive charges. This suggests either overmeasurement of cations, undermeasurement of anions, the presence of unmeasured anions, or some combination of these factors. DOC averages about 1.4 mg/l in these samples, so organic anions may account for at least part of this deficit. Another possibility is the presence of some of the Ca, Mg, Na, or K in complexed form in the samples, which would lead to overmeasurement of these cations. Since these species are determined by atomic absorption, the reported values represent total elemental and not ionic concentration.

The use of field pH to calculate theoretical conductance (see section 3.3.2) may account for some of the deviation of these values from those measured, since the calculated conductance depends more on H concentration than on any other parameter. Nevertheless, results of this analysis are consistent with the charge balance calculations. Distributions are approximately normal, with means less than zero for all years except 1983. This suggests the presence of an unmeasured or undermeasured ion which contributes to the measured conductance but is not included in the theoretical value. The contribution of DOC to the conductance is not included in the calculation, but whether this accounts for the observed discrepancy is impossible to determine. Taken together with the charge balance results, these analyses suggest that some minor constituents are unanalyzed.

Both charge balance and calculated conductance provide effective means of screening for transmission and recording errors in the database, and will help in identifying problems with analytical data.

5. QA/QC IMPROVEMENTS FOR 1988:

5.1. Data Management

During the summer of 1988, the entire project database is being transferred into the INGRES database management system. All results of chemical analyses will be reloaded from the USGS WATSTORE database as part of this process. The new data tables will include flags for detection limits and values with poor charge balances or calculated conductance, the number of significant digits in each value, and the date of analysis wherever possible.

As part of the database transfer, new programs are being written for the downloading of USGS data. These will include extensive checks of data quality using charge balance, conductance, and outlier criteria. Any new analyses which fail these tests will result in reanalysis of the sample by the USGS. Formal criteria will be developed to decide whether to accept data from reanalyzed samples or keep the original analysis.

New data tracking procedures are being developed so that all analyses are recorded and evaluated before the six month reanalysis deadline. These will include a means to notify project personnel whenever a sample analysis is behind schedule so that efforts to retrieve the data may be initiated well before it becomes too late to request reanalysis.

5.2. QA/QC Procedures

A new QA plan will be developed and implemented by the end of 1988. This will include specific data quality objectives (DQO's) by which the data will be evaluated in the future.

The collection of duplicate samples for precision analysis will be expanded. The current practice of collecting co-located samples is crucial to evaluate the total uncertainty involved in all parts of the sample collection, handling, and analysis process and will continue. New efforts will be initiated to quantify the amount of error introduced at each step of the process. Sample splits will be prepared in the field laboratory before samples are processed. This will allow the variance due to sample processing and analytical uncertainty to be subtracted from the total variance, providing an estimate of the true natural variation in the composition of the water in the field. Reanalysis of some samples at random will allow quantification of the purely analytical uncertainty.

Since imprecision in the data adds in quadrature [9], the total uncertainty is driven by the most uncertain component. Expanded analysis of sample splits and duplicates from each step of the measurement process will thus allow identification of the most important component in the overall uncertainty. Efforts can then be directed to solve problems with this component to achieve the stated DQO's.

More blanks will be collected and analyzed. Blanks will be analyzed from each step in the sample handling process (ie peristaltic pump, sampling bottle, filter pump, etc) to identify any source of contamination which may be present.

A comparability study will be undertaken to examine differences between labs used by all project collaborators. Samples or artificial solutions will be distributed to these labs and analyzed in a 'round robin' approach. This study will include the USGS Lab, the Soils Testing Lab at CSU, the Department of Geology and Geophysics lab at the University of Wyoming, and the Department of Natural Resources lab at Cornell University.

Smaller studies within the project will have better QA/QC coordination in the future so that data generated this way can be incorporated into the larger database. Each study will be required to submit a QA plan to ensure that it meets the projects DQO's.

The calculations included in this report will be repeated once the database has been reloaded from WATSTORE. These updated calculations will appear in the project's Annual Report for FY 1988. All future Annual Reports will include a summary of QA/QC improvements for that year, tables of precision, charge balance, conductance statistics, and external audit results.

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