

**QUALITY ASSURANCE REPORT**

Loch Vale Watershed Study, 1989-90

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May 22, 1991

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## List of Acronyms

ANC	Acid Neutralizing Capacity, equivalent to alkalinity
CAL	Central Analytical Laboratory at the Illinois State Water Survey
DAMS	Data Acquisition and Monitoring Subsystem
DOC	Dissolved Organic Carbon
DQO	Data Quality Objectives
GOES	Geostationary Operational Environmental Satellite
IPD	Ion Percent Difference
NADP	National Atmospheric Deposition Program
NOAA	National Oceanic and Atmospheric Administration
NPS	National Park Service
RSD	Relative Standard Deviation
STL	Soil Testing Laboratory
USGS	U. S. Geological Survey
WEBB	Watershed Energy Biogeochemical Budgets, USGS program

## **Introduction**

The Loch Vale Watershed Study was initiated by the National Park Service in 1980 and has continued as a long term monitoring site since then. The watershed also is currently in the Watershed Energy Biogeochemical Budgets program of the U.S. Geological Survey and is a proposed site for the Global Change research program of the NPS. Data quality through 1987 was assessed in an earlier report [3], and 1988 data was reviewed in the 1988 Annual Report [2].

There are four areas of ongoing long term data collection; meteorology, hydrology, precipitation chemistry, and surface water chemistry. Each of these types of data will be discussed separately below. Additional types of data such as lake bathymetry, soil characteristics, and various student research projects are collected on an individual project basis. Data are reviewed and stored on a Unix based local computer network at the Natural Resource Ecology Laboratory (NREL) at Colorado State University.

A primary objective of the long term program is to detect and interpret trends over multi-year periods, taking into account seasonal and annual variation. To meet this objective, an accurate and regular assessment of data quality is important. This report addresses the quality control procedures and the quality of analytical results for the Loch Vale data from 1989-90.

## **Meteorological Data**

Meteorological data for the Loch Vale watershed are collected by a solar powered remote area weather station. The following parameters are measured: wind speed, wind direction, relative humidity, barometric pressure, solar radiation, air temperature and precipitation amount. Data are gathered every 15 minutes by a Handar 524 data collection platform, and relayed hourly to NOAA's Wallops Island, VA, ground station via the GOES West satellite. Quality assurance is maintained with an annual calibration check performed by Environmental Technology, Inc., to maintain the equipment within published limits. The

Data Acquisition and Monitoring Subsystem (DAMS) at the Wallops Island downlink monitors each hourly data transmission for signal strength (EIRP), frequency offset, modulation index and received data quality [6]. Fifty randomly selected hourly transmissions from the 1990 data were analyzed for each of these parameters (Table 1). All parameters except EIRP were always within the normal range. EIRP is slightly lower than normal in one out of four transmissions, however, in the absence of other problems the observed range does not affect the transmitted signal [6].

**Table 1: Meteorological data signal quality parameters**  
 Summary statistics from 50 randomly selected data transmissions  
 Wallops Island DAMS provides these signal quality measures each hour

	Signal Strength (EIRP)	Frequency Offset (Hz)	Modulation Index	Data Quality
mean	44.1	+47	always Normal ( $60^{\circ} \pm 5^{\circ}$ )	always Normal (error rate $< 10^{-6}$ )
SDs	2.1	41		
normal range	44 to 49	-250 to +250		
# outside normal	12 low	0		

### Hydrological Data

Surface water flow out of the Loch Vale Watershed is gaged in Icy Brook, just below the outlet from the Loch. A Parshall Flume with a stilling well was installed in 1983. Stage height data are collected both electronically and mechanically when there is measurable flow through the flume, typically from May through October. A continuous flow record has been kept since Oct 15, 1983, with an Omnidata electronic stage height recorder and a Leupold and Stevens chart recorder. Field verification of the recorded gage heights occur weekly. Annually, data are approved by comparing the electronic, chart and field data. Any discrepancies are corrected according to the information at hand. These corrections are noted and stored along with the data files at NREL. The data are converted to flow (in  $m^3 \text{ sec}^{-1}$ )

using a rating formula provided by the Thompson Pipe and Steel Co. According to Winter [12], the accuracy of Parshall Flumes is  $\pm 5\%$ . In Loch Vale, it is estimated that an additional 5% uncertainty is introduced by water flowing around or under the flume structure.

## **Precipitation Data**

The Loch Vale Watershed Study participates in the National Atmospheric Deposition Program (NADP), which is responsible for the analysis of precipitation chemistry and the quality assurance of those data. The network has a published quality assurance plan [1] and a report is produced periodically by the Central Analytical Laboratory (CAL) which gives the results of their quality control projects. The NADP goals for laboratory measurements of specific analytes are given in Table 2. The most recent CAL report covers data from 1989 [7]. It states that CAL was meeting these goals through a quality control program of weekly blanks, quality control check samples, blind network sample replicates, and an internal blind audit with artificial samples.

The precipitation data for the Loch Vale site, CO98, have been verified and published by NADP through June, 1990. Nine weekly samples since 1989 have been considered invalid; twice for contamination, once because of a two week sampling interval when a winter storm curtailed field activities, and six times because of insufficient sample volume when there was significant precipitation during the week. The latter cases all occurred in the winter season. The standard Aerochem Metrics Precipitation Collector used by the network is poor for catching dry snow under the windy conditions prevalent in Loch Vale in the winter. This problem has been discussed with the NADP technical staff, but currently there is no known solution.

Field personnel are responsible for measuring pH and conductivity of weekly precipitation samples. Each analysis is accompanied by measurement of a quality control check sample. If pH is not within 0.1 unit and conductivity within 4  $\mu\text{S}/\text{cm}$  of the reported check sample values, the equipment is re-calibrated. The field technicians also participate twice per year in an intersite comparison organized by the USGS. An artificial sample is sent to each NADP site for measurement of pH and conductivity. Measurements are expected to

be within the weekly criteria (above) of the network wide median values. In 1989-90, as in all previous years, lab results met NADP quality assurance criteria (Table 3).

**Table 2: Data Quality Goals for Precipitation Chemistry**  
From NADP/NTN Quality Assurance Plan, 1990 [1]

Analyte	Units	Bias/Precision	Detection Limit
Ca	mg/l	100% at Detection Limit  20% at 10 times Detection Limit  10% at 100 times Detection Limit	.009
Mg	mg/l		.003
Na	mg/l		.003
K	mg/l		.003
NH <sub>4</sub>	mg/l		.02
SO <sub>4</sub>	mg/l		.03
NO <sub>3</sub>	mg/l		.03
PO <sub>4</sub>	mg/l		.02
Cl	mg/l		.03
pH < 5.0			±0.1 / ±0.03
pH > 5.0		±0.3 / ±0.1	
Specific Conductance			
10 - 100	µS/cm	±10% / ±3%	
>100	µS/cm	±6% / ±2%	

**Table 3: USGS Intersite Laboratory Comparison**  
Artificial sample sent to field sites on dates shown  
Median values from all participating NADP sites  
Measured values from Loch Vale field laboratory

Date	Median pH	Measured pH	Median Conductance	Measured Conductance
3/89	4.68	4.69	8.6	9.3
9/89	4.01	4.04	43.2	44.5
4/90	4.57	4.60	12.3	12.8
10/90	4.85	4.88	6.5	6.6

## Surface Water Chemistry

### Introduction

Surface water samples are routinely collected throughout the Loch Vale Watershed, with a major emphasis on weekly samples from The Loch outlet as long as there is sufficient flow. Specific quality control procedures for the collection and handling of samples before shipment for chemical analysis have been described previously [3] and follow established protocol for low ionic strength waters, e.g. [9]. Chemical analysis of surface water samples was done by the USGS Central Laboratory, in Arvada, CO, through March 1989. With an overlap period starting in Jan 1989, analyses were performed by the Soil Testing Laboratory (STL) at Colorado State University through Aug 1, 1989. It was thought this change would provide more direct oversight of sample analysis, faster turnaround time and lower cost. However, results from this lab were not satisfactory and sample analysis reverted to the USGS Central Laboratory starting Aug 8, 1989.

Each laboratory is responsible for its own internal quality assurance, according to current standards for analysis of low ionic strength natural waters, e.g. [5]. This information is not published, but precision estimates are included in the Services Catalog for the USGS Central Laboratory [4]. Both the USGS Laboratory and the STL participated in a round robin interlaboratory comparison in 1989. A variety of samples were distributed to participating laboratories. Analytical results were compiled by USGS personnel. Ratings were given to each laboratory according to the closeness of its measured values for a series of parameters to the mean values for all laboratories. Both laboratories received satisfactory to excellent ratings, depending on the sample [8,11].

Overall data quality for combined field and lab procedures is assessed through a series of replicate and blank samples. The aim is to meet the same goals already established for precipitation (Table 2), although the laboratories have higher detection limits for surface waters, due to the use of different analytical techniques. Bias and contamination due to field procedures are estimated using blank samples. In LVWS, blank samples are deionized water (conductivity  $< 1.0 \mu\text{S/cm}$ ) which is carried up to the field site, then "sampled" according to standard procedures. Precision is estimated using two types of replicate samples. Duplicate



samples are collected in separate bottles from the same site within minutes of each other. Split samples are collected in a single large bottle in the field, then split during the field lab processing. Both types are treated as separate regular samples for shipment to the laboratory for analysis.

Analytical results are screened to detect problems with individual samples. The difference between the sum of the cations and the sum of the anions, divided by the total ion concentration (ion percent difference, IPD) is used as a general indicator of analytical difficulties. Individual analyte concentrations of samples with IPD > 10% are compared with expected values to identify specific analytical errors, and reanalysis of these analytes is requested if possible.

#### Results from the USGS Central Laboratory

There were eight duplicate pairs, and six split pairs of samples analyzed by the USGS lab in 1989-90 (Table 4). The difference between the duplicate sample means and the split sample means reflects seasonal change. Precision is assessed by examining the difference in measured concentration within sample pairs. A t-test was used to compare the mean difference of duplicate sample pairs against the mean difference of split sample pairs for each analyte. No significant differences were found between the two sample types. Since any differences between the duplicate and split samples would be a result of the field collection procedure, it is concluded that in general, such procedures do not add variability to the surface water data, or in other words, data precision is not affected by the techniques used to collect samples in the field.

The duplicate and split sample results are combined to provide a more accurate estimate of data precision (Table 5). Given a narrow sample concentration range or no relationship between variance and mean, conditions which generally apply to Loch Vale samples [3], the relative standard deviation ( $100 * (\text{std dev}/\text{mean})$ , RSD) is the most useful statistic for comparing precision among different analytes. Both iron and aluminum had single sample pairs with much higher concentration and variance than other sample pairs; those data are not included. Other missing data are due to incomplete laboratory analyses.

For most analytes, the USGS data meet data quality goals for precision. When the RSD is high for an analyte, mean concentration is near the analytical detection limit. The variability of pH measurement slightly exceeded DQO. Dissolved Organic Carbon (DOC) showed the worst RSD, while the mean DOC was more than 10 times the detection limit. Two sample pairs with large differences are primarily responsible for the large standard deviation, indicating a problem with occasional contamination.

**Table 4. Replicate samples analyzed by USGS Central Lab**

Values are for sample pairs collected at same site and time  
 $H_0$ : Duplicate pair mean differences are not different than split pair mean differences  
 Duplicate pair n = 8, Split pair n = 6  
 Major ions and DOC are in mg/l; Al, Fe, and Mn are in  $\mu\text{g/l}$   
 Conductivity is in  $\mu\text{S/cm}$ , ANC is in  $\mu\text{eq/l}$

	Duplicate pairs			Split pairs			ttest
	mean	SDs	mean diff.	mean	SDs	mean diff.	p =
Ca	2.016	0.027	0.014	1.143	0.043	-0.006	0.522
Mg	0.305	0.003	0.001	0.175	0.007	0.002	0.823
Na	0.815	0.031	-0.007	0.395	0.048	-0.034	0.430
K	0.202	0.006	0.001	0.130	0.000	0.000	0.734
NH <sub>4</sub>	0.008	0.004	-0.001	0.010	0.003	-0.002	0.607
SO <sub>4</sub>	2.454	0.085	0.006	1.410	0.055	0.06	0.404
NO <sub>3</sub>	0.763	0.035	0.031	0.895	0.063	-0.035	0.117
PO <sub>4</sub>	0.007	0.003	0.001	0.009	0.005	0.004	0.378
Cl	0.203	0.021	0.02	0.096	0.000	0.000	0.102
F	0.104	0.012	-0.01	0.094	0.011	0.000	0.296
SiO <sub>2</sub>	1.743	0.005	-0.003	1.454	0.082	0.052	0.703
Al	14.4	4.54	-0.4	39.9	9.32	2.5	0.623
Fe	88.5	12.00	-2.3	141.4	47.60	-21.1	0.473
Mn	9.8	1.67	-0.7	2.2	0.40	0.1	0.226
DOC	2.77	5.785	-3.29	1.64	1.664	-1.28	0.645
ANC	93.2	10.28	-4.7	58.2	13.90	7.3	0.229
Cond	19.8	0.36	-0.04	14.1	0.07	-0.03	0.986
pH	6.692	0.211	0.059	6.543	0.065	0.027	0.814

**Table 5. Overall Precision and Bias for the USGS Central Lab**

Values for pooled duplicate and split sample pairs from Table 4

Units the same as in Table 4

SDs = sample standard deviation

RSD (relative std. dev.) =  $(100 * (\text{std dev} / \text{mean}))$ 

Detection limits as reported in analytical results from USGS Central Laboratory

Average minimum values from all 1987-1990 data excluding outliers

Bias % =  $(100 * (\text{mean blank conc}(\text{from pre-1988 data}) / \text{average minimum}))$ 

† = at or below detection limit

	Combined Replicate Pairs				detection limit	avg. min.	Bias %
	mean	SDs	RSD	n			
Ca	1.652	0.035	2.1	12	.02	1.0	8
Mg	0.251	0.005	1.9	12	.01	.13	22
Na	0.640	0.039	6.1	12	.02	.27	81
K	0.172	0.005	2.7	12	.01	.10	10
NH <sub>4</sub>	0.008	0.004	41.9	12	.003	†	333
SO <sub>4</sub>	2.019	0.074	3.7	12	.01	1.1	2
NO <sub>3</sub>	0.818	0.049	5.9	12	.01	.6	7
PO <sub>4</sub>	0.008	0.004	55.9	11	.003	†	200
Cl	0.158	0.016	10.3	12	.01	.07	30
F	0.100	0.011	11.4	12	.01	.05	36
SiO <sub>2</sub>	1.623	0.053	3.3	12	.01	1.3	14
Al	18.5	3.33	18.0	13	1	13	88
Fe	75.9	5.04	6.6	13	10	23	22
Mn	6.6	1.30	19.7	12	1	†	110
DOC	2.36	4.723	200.2	11	.1	0.8	25
ANC	78.2	11.97	15.3	14		35	14
Cond	17.4	0.28	1.6	14		10	40
pH	6.628	0.165	2.5	14		-	-

The previous Quality Assurance Report examined the bias in Loch Vale samples analyzed by the USGS Laboratory from blank samples collected prior to 1988 [3, Table 3]. No blank samples were sent to the USGS Laboratory in 1989-90. In the earlier blanks, most analytes were close to the detection limits, indicating minimal field contamination. However, calcium, ammonium, silica, aluminum and conductivity had high variances, indicating

occasional contamination. Sodium concentrations were consistently higher than detection limits, indicating a possible bias due either to field or laboratory procedures. Although it is not readily apparent from Loch Vale blanks, chloride values for all samples analyzed by the USGS Central Laboratory prior to 1988 exhibit a small positive bias due to a calculational error. Instructions for correcting this error are forthcoming from the USGS. The percent bias presented in Table 5 is produced by dividing the mean blank concentration by the average annual minimum concentration (from scanning the 1987-1990 data). Most analytes met the data quality objectives (DQO) in Table 2 for bias. Since the average minimum calcium concentration was high, bias was low even though the blank was relatively high. Sodium, silica, aluminium and conductivity biases were greater than DQO. Both ammonium and phosphate also show a large bias, but minimum values were consistently below detection and thus a small blank value had a large effect.

The mean ion percent difference of 1989-90 samples (Figure 1) is slightly more positive than in 1988 data [2, Figure 7]. This may be due to an undermeasurement of alkalinity in 1990 samples. In March 1990, the laboratory building had structural problems which resulted in delayed analysis of samples from March and April. Because it must be performed on unfiltered, unpreserved aliquots, alkalinity is time-sensitive and is difficult to reanalyze accurately. Samples from June-August 1990 were also analyzed with techniques suitable to higher alkalinity waters, which resulted in the underestimation of the significant but low alkalinities of Loch Vale waters. All samples are now flagged for low alkalinity analysis.

#### Results from the Soil Testing Laboratory

The results from both paired replicate samples and blank samples sent to the STL are presented in Table 6. Six blank samples were analyzed. Relatively high values for mean and standard deviation were found for calcium, sodium, potassium, chloride, and aluminum. These reflect a few samples with high values, indicating a problem with occasional contamination. Percent bias was still acceptable for calcium, due to a high annual minimum value, and for aluminum, due to a detection limit for STL data ten times that for USGS data. Percent bias

for sodium and potassium was close to, but greater than DQO while chloride clearly exceeded those goals. Ammonium, iron and alkalinity had high mean values with relatively low standard deviations, indicating either consistent contamination or accuracy problems with the analytical methods. All these analytes exceeded DQO for percent bias. Nitrate, phosphate, fluoride and manganese were always at detection limits, which were higher than the corresponding USGS limits. Since annual minima for ammonium, phosphate and manganese

**Table 6. Replicates and Blanks Analyzed by the Soil Testing Lab**

Replicate pairs, n = 7, Blanks, n = 6

Units as in Table 4

SDs = sample standard deviation

RSD = relative standard deviation as in Table 5

Bias % calculated as in Table 5

‡ = STL detection limit higher than USGS, annual minima below detection

	Replicate Pairs			Blanks			Bias %
	mean	SDs	RSD	mean	SDs	RSD	
Ca	1.559	0.079	5.1	0.079	0.083	105.6	8
Mg	0.274	0.005	1.7	0.020	0.000	0.0	15
Na	0.665	0.020	3.0	0.086	0.145	169.4	32
K	0.195	0.033	16.7	0.053	0.093	175.0	53
NH <sub>4</sub>	0.196	0.369	188.0	0.083	0.035	41.9	‡
SO <sub>4</sub>	2.764	0.180	6.5	0.040	0.041	103.1	4
NO <sub>3</sub>	0.313	0.085	27.0	0.044	detection limit		7
PO <sub>4</sub>	0.031	detection limit		0.031	detection limit		‡
Cl	0.386	0.030	7.8	0.176	0.179	101.8	251
F	0.054	0.007	12.1	0.010	detection limit		20
SiO <sub>2</sub>	1.165	0.043	3.6	0.060	0.060	99.5	5
Al	30.0	5.86	19.5	12.4	15.404	123.9	92
Fe	177.1	25.36	14.3	22.9	17.043	74.6	100
Mn	32.9	0.00	0.0	10.0	detection limit		‡
DOC	4.15	4.857	117.0	incomplete lab results			-
ANC	59.9	3.66	6.1	19.6	13.37	68.2	56
Cond	15.4	1.28	8.3	1.6	0.79	50.0	16
pH	6.329	0.065	1.0	-	-	-	-

were at the USGS detection limits, the higher limits for STL data represent a substantial loss of information. Sodium, silica and conductivity were improved from USGS results, although sodium and conductivity still did not meet DQO.

Seven replicate sample pairs were analyzed for an overall estimate of precision. In contrast to the USGS results, ammonium, nitrate and conductivity did not meet DQO, although the latter two were close. Ammonium is difficult to measure at low concentrations and may be expected to give problems for a lab just beginning analysis of low ionic strength waters. The STL analyses of DOC were more variable than desired, similar to the USGS results.

The distribution of IPD for the STL (Figure 2) shows both a greater standard deviation and a substantially lower mean than any previous USGS data. This suggests both a consistent problem with overmeasurement of anions or undermeasurement of cations, and precision problems with regular samples. A specific problem was the time lapse between shipment of samples and receipt of analytical results. This inhibited timely review of the data and subsequent chances for reanalysis.

### Comparison of USGS Central Laboratory and STL Results

Various differences in the quality control samples analyzed by the USGS Central Laboratory or the Soil Testing Laboratory have been covered above. Plots of regular sample concentrations from March 1987 to August 1989 (spanning both the USGS lab and the STL analytical periods) reveal several patterns. For some of the analytes the mean concentrations and seasonal patterns are consistent through both the USGS and STL data (e.g. sodium, Figure 3) though often the STL data don't hold as tightly to the seasonal trends (e.g. DOC, Figure 4). These include DOC, silica, aluminum, iron, alkalinity and pH. STL results for some other analytes follow USGS data quite closely except for a number of outliers, both high (sulfate, Figure 5) and low (magnesium, Figure 6). For ammonium (Figure 7) and manganese, STL's detection limit is too high for Loch Vale waters. Almost all USGS data is below that limit, and STL data occasionally are very high. Nitrate (Figure 8) and potassium

have a large range and no seasonality in STL data compared to the previous USGS analyses. Overmeasurement of anions occurs generally and is especially pronounced in chloride (Figure 9). This is probably what accounts for the low mean and high variability of the IPD data.

In Jan - Mar 1989, six pairs of samples were sent to both laboratories for analysis. A pairwise t-test was used to test whether the mean difference within sample pairs was different from zero (Table 7). If the mean difference is positive, the USGS concentration is higher, a negative value indicates that the STL concentration is higher. Eight analytes showed significant differences. Calcium, sodium and conductance were positive, silica, ammonium, aluminum, manganese and pH were negative. The results for sodium, silica and conductance are consistent with the bias estimates, indicating an improvement in STL over USGS, although this is not clear from the timeplots (Figure 3, for sodium). Ammonium and manganese are also consistent with previously discussed results. The STL produced high values and had high detection limits for these analytes (Tables 5 and 6, Figure 7 for ammonium). Bias estimates and timeplots for calcium, aluminum and pH did not suggest a consistent difference between USGS and STL results, although blanks for aluminum were high for both laboratories (Tables 5 and 6).

### Surface Water Chemistry Overview

A summary of the different data quality measurements for each analyte is presented in Table 8. In general, surface water data for 1989-90 meet or are close to data quality goals. Four analytes exhibited problems in the data produced by both the USGS Central Laboratory and the Soil Testing Laboratory. Sodium, ammonium, phosphate and conductivity field blanks were higher than DQO. Ammonium and phosphate usually occur at very low concentrations in Loch Vale waters. These analyses are particularly sensitive to contamination and in part the problem may be due to the difficulty in removing all ammonium and phosphate from the deionized water used for blank samples. Deionized water with conductance  $< 1 \mu\text{S}/\text{cm}$  may have a total electrolyte concentration of .2-.5 mg/l [10]. Contamination in the water used for blanks could easily account for the observed biases if the concentration of ions is not distributed evenly among the chemical species analyzed. The sodium blanks decreased

with the change in analytical laboratories, possibly indicating a relationship to analytical method. High conductance is probably a reflection of the high blanks for other analytes. Poor precision for DOC analysis is due to just a few samples with high values. The duplicate sample standard deviation was much higher than that for split samples (Table 4), although statistically they were not different. Perhaps this indicates that field procedures are the most likely source of occasional DOC contamination.

**Table 7. Pairwise Comparison of USGS and STL Replicated Pairs**  
 Values are for replicate sample pairs, one of which was sent to the USGS Central Laboratory for analysis, the other sent to the Soil Testing Laboratory  
 $H_0$ : Pairwise mean difference is not different from 0

\*  $p(t) < .05$   
 \*\*  $p(t) < .01$

		n	Difference		pair-wise t-test		
			mean	SDs	t =	p =	
Ca	mg/l	6	0.332	0.197	4.117	.049	*
Mg	mg/l	6	0.005	0.030	0.415	.695	
Na	mg/l	6	0.122	0.042	7.151	.001	**
K	mg/l	6	0.008	0.051	0.399	.706	
NH <sub>4</sub>	mg/l	4	-0.068	0.012	-11.282	.002	**
SO <sub>4</sub>	mg/l	6	-0.597	1.254	-1.165	.296	
NO <sub>3</sub>	mg/l	5	-0.195	0.195	-2.239	.089	
Cl	mg/l	6	-0.307	0.436	-1.722	.146	
F	mg/l	4	0.038	0.028	2.724	.072	
SiO <sub>2</sub>	mg/l	6	-0.198	0.185	-2.629	.047	*
Al	μg/l	6	-23.7	12.80	-4.529	.006	**
Fe	μg/l	6	-20.7	21.87	-2.315	.069	
Mn	μg/l	6	-4.7	1.86	-6.139	.002	**
DOC	mg/l	6	-0.23	2.836	-0.202	.848	
ANC	μeq/l	6	27.3	36.55	1.827	.127	
Cond.	μS/cm	6	1.9	1.57	2.990	.031	*
pH		6	-0.19	0.13	-3.562	.016	*



The change in analytical laboratories was the most significant event for surface water data quality. Analysis of blanks and replicates indicated that most analytes still met DQO. STL data showed a reduction in bias for sodium, silica and conductivity analyses. However, blanks were worse for potassium, iron, alkalinity and especially chloride. Filtration procedures and analytical methods were slightly changed for STL samples. It is likely these were responsible for the changes in blank values, though it is unknown why the chloride values were so much worse. Precision declined greatly for ammonium, less so for nitrate and conductivity, and was slightly improved for pH. Laboratory handling may be responsible for some of these changes. Clearly there were methodological problems with the ammonium analysis. Some of the results from the interlaboratory comparison samples (Table 7) agreed with the blank sample results (sodium, ammonium, aluminum and conductivity), while others were contradictory (silica) or unexpected (calcium, manganese and pH) compared to the blank samples. The number of samples may have been too small to expect both the blanks and the comparison samples to give congruent results. Plots of concentration versus time for regular samples (Figures 3 - 9) were the most useful method for revealing inconsistencies in the results produced by the different laboratories. The STL data for most analytes was similar to, though more variable than the USGS data. However, a number of analytes varied markedly between the laboratories. Taken all together, the usefulness of the STL data is highly questionable, though with careful screening some of it may be acceptable for certain purposes. Currently all STL produced data are stored separately and not used in the main Loch Vale database.

## **Future Plans**

Quality assurance of long-term data from the Loch Vale Watershed Study is essential. Quality control procedures already implemented will continue for all four areas of data collection. These are seen as adequate for the meteorological and precipitation chemistry data. Through closer association with the U.S. Geological Survey WEBB program, it is hoped that there will be increased accuracy and precision of the hydrological data. Surface water data quality control will continue to require collection of replicate and blank samples.

as well as careful screening of analytical results. This latter aspect will be improved through streamlining of computer data handling procedures and the frequent construction of timeplots for all analytes. It is also planned to coordinate data formats and quality assurance with standards for sites in the Long Term Ecological Research network funded by the National Science Foundation.

**Table 8. Summary of Surface Water Data Quality**

see text for explanation of data quality measures

pre. = precision

? = close to, but exceeding DQO

\* = did not meet DQO

> = USGS values greater than STL values

comments under timeplots refer to STL data compared to USGS data

	USGS		STL		USGS vs. STL	
	bias	pre.	bias	pre.	pairs	Timeplots
Ca					>	
Mg						low outliers
Na	*		?		>>	
K			?			no ann. pattern
NH <sub>4</sub>	*		*	*	<<	high det. limit
SO <sub>4</sub>						high outliers
PO <sub>4</sub>	*		*			high det. limit
NO <sub>3</sub>				?		high & no pattern
Cl			*			high & variable
F						
SiO <sub>2</sub>	?				<	
Al	*				<	high det. limit
Fe			*			
Mn					<	high det. limit
DOC		*		*		more variable
ANC			*			
Cond.	*		?	?	>	
pH		?			<	

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Figure 1. USGS Data  
1 Jan 1989 - 20 Aug 1990

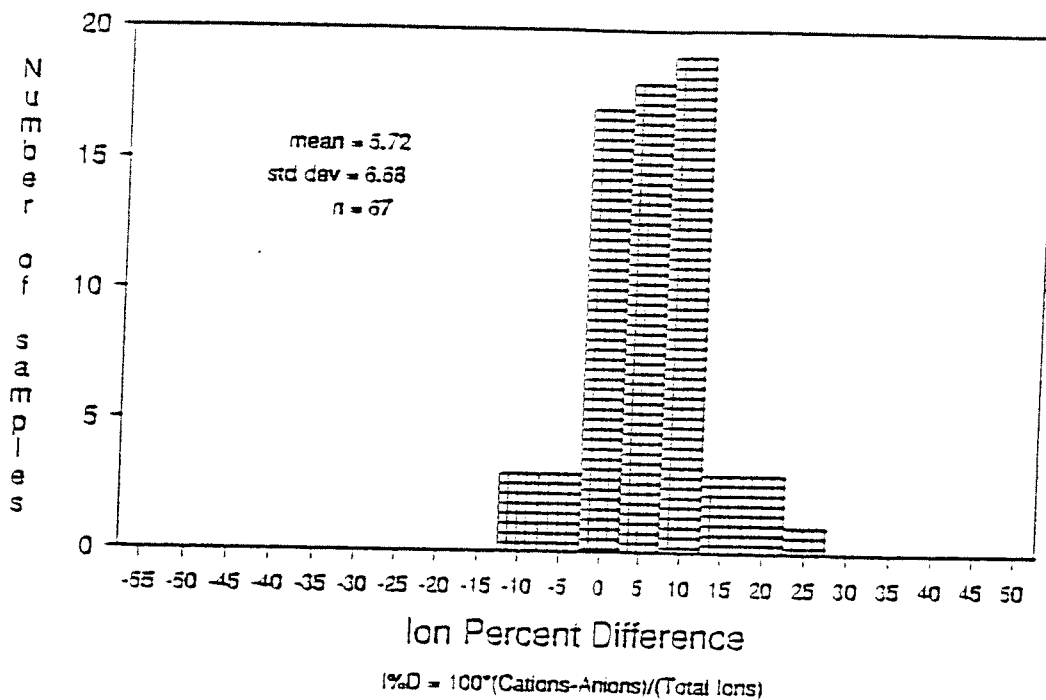
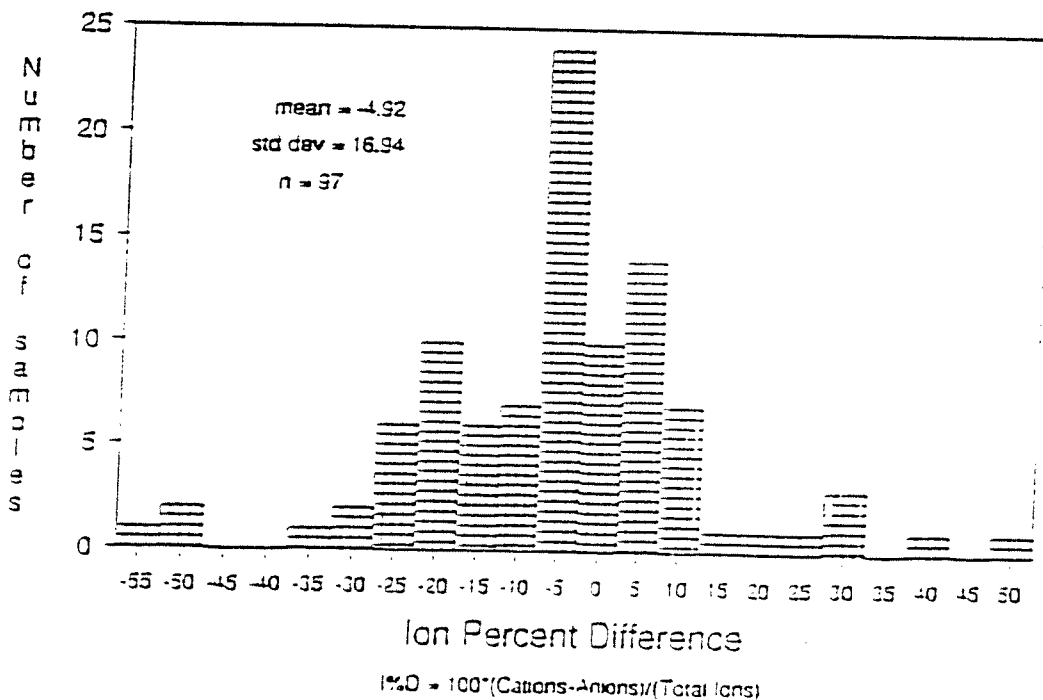
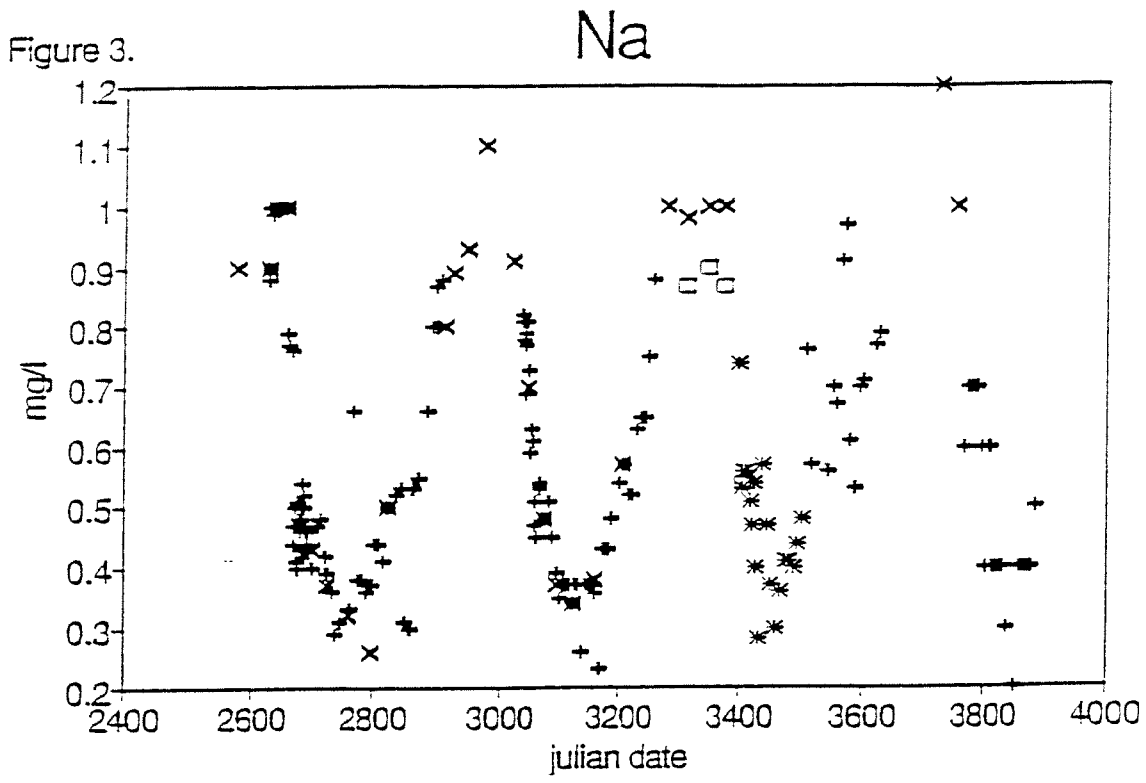


Figure 2. STL Data  
1 Jan 1989 - 1 Aug 1990





+ outlet(usgs) \* outlet(std) □ surface(std) x surface(usgs)

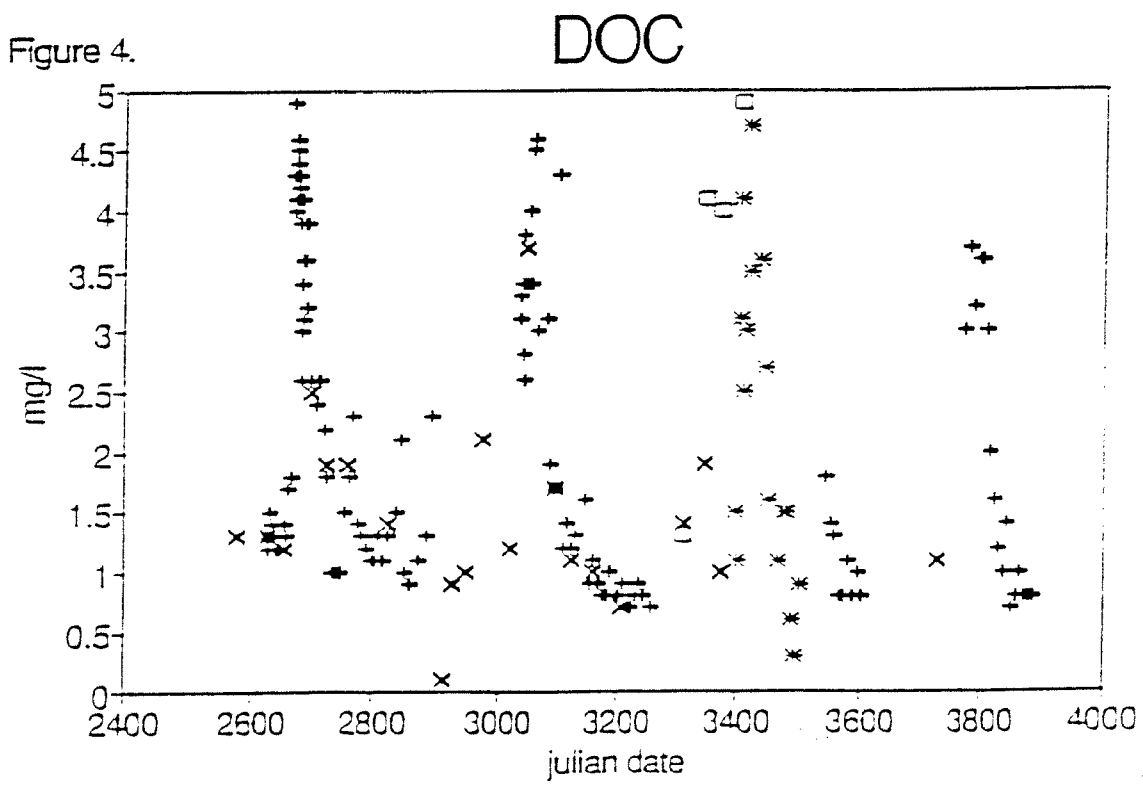
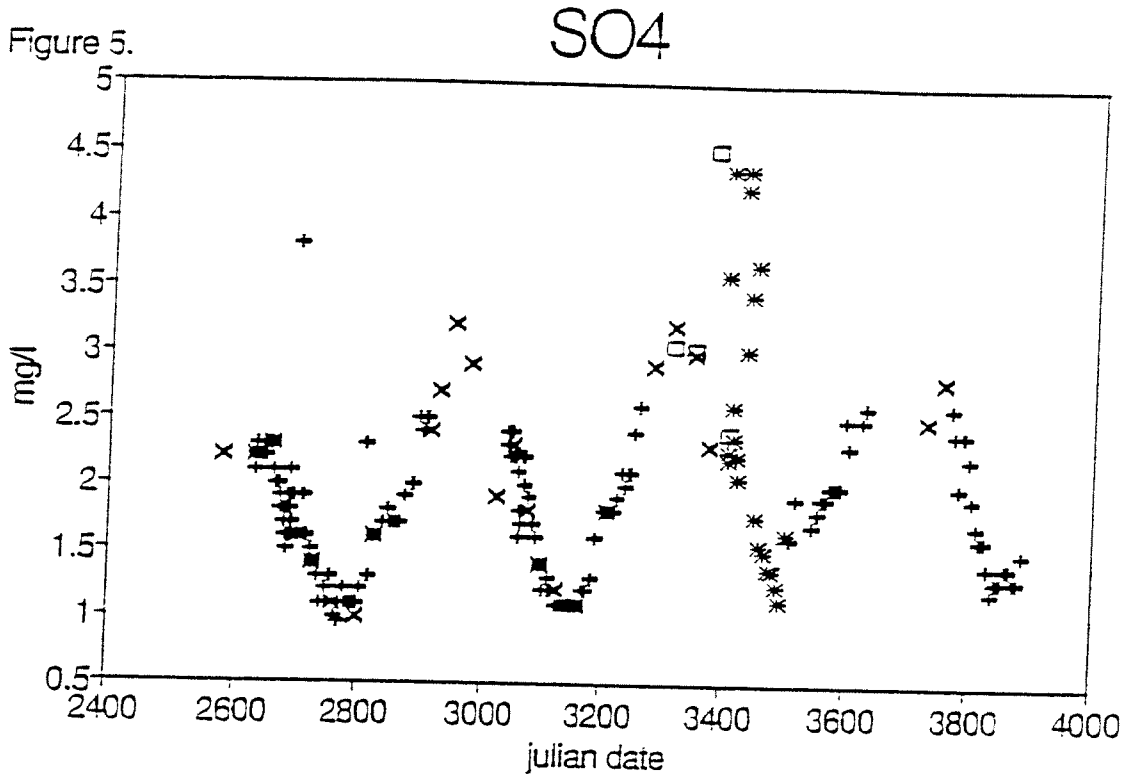


Figure 5.



+ outlet(usgs)   \* outlet(stl)   □ surface(stl)   x surface(usgs)

Figure 6.

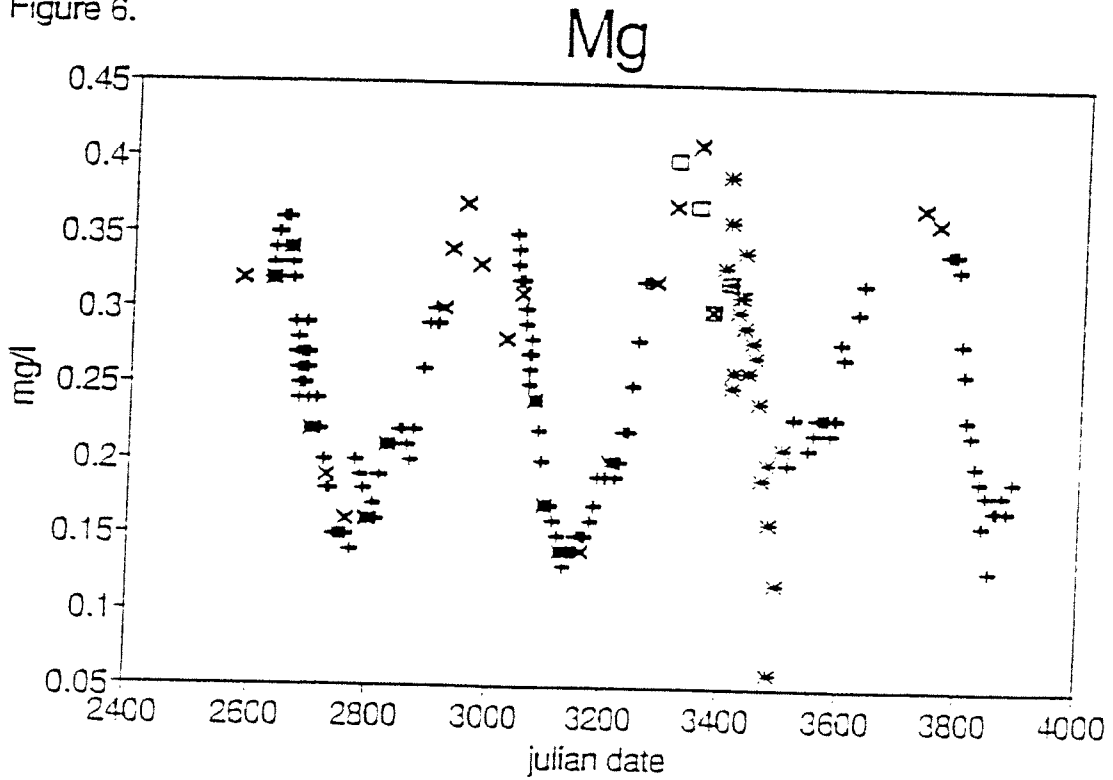
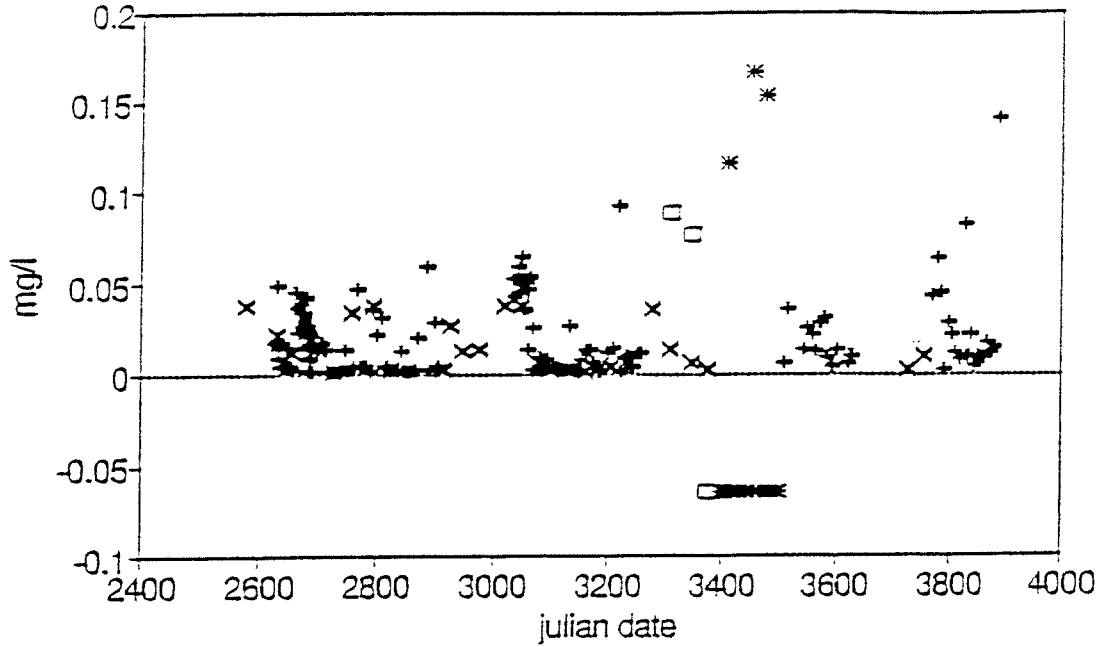


Figure 7.

NH4

-.064 = below detection limit



+ outlet(usgs) \* outlet(stl) □ surface(stl) x surface(usgs)

Figure 8.

NO3

-.044 = below detection limit

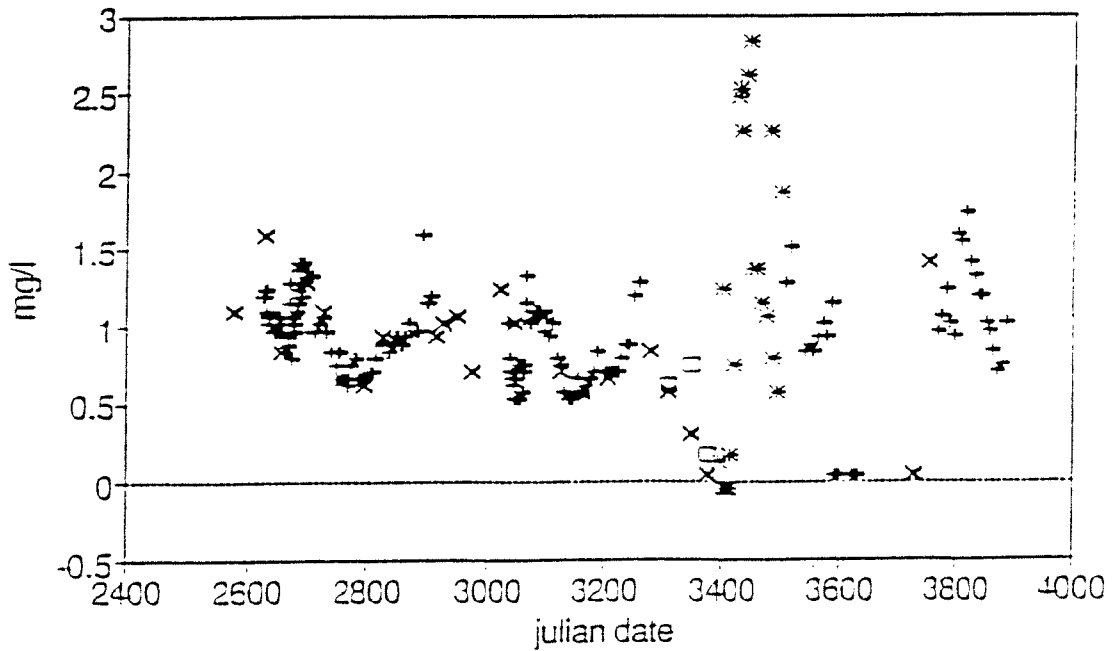
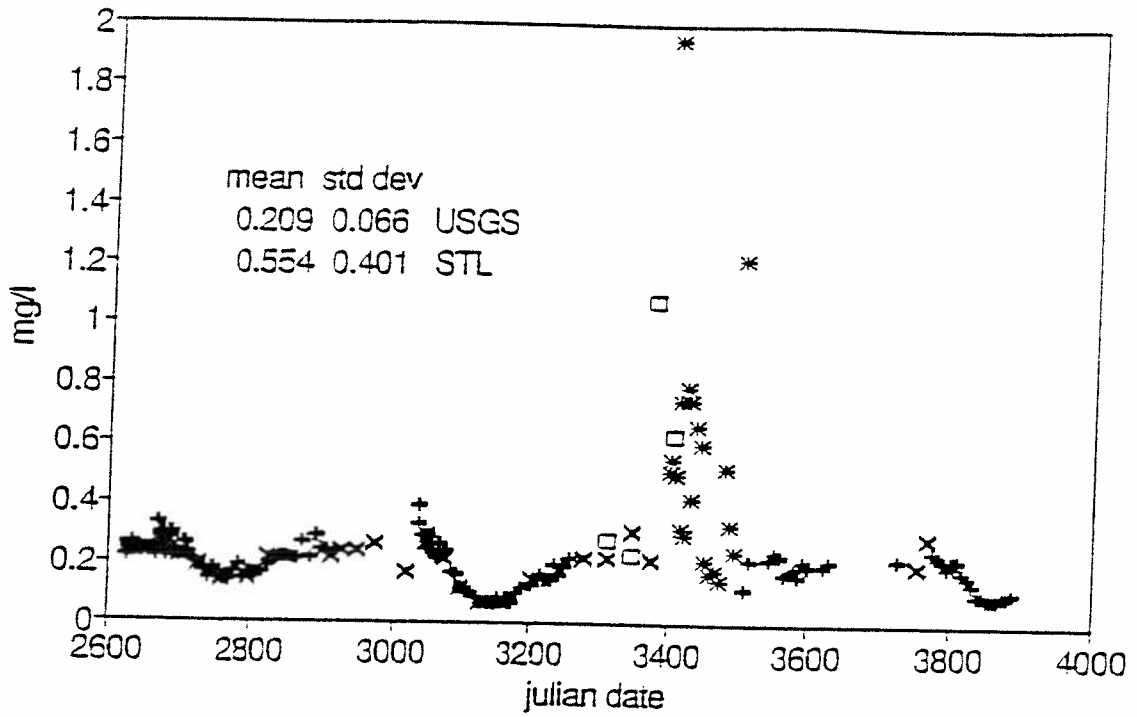




Figure 9.

Cl



+ outlet(usgs) \* outlet(stl) □ surface(stl) x surface(usgs)

