VARIABILITY IN WET ATMOSPHERIC DEPOSITION DATA DETERMINED WITH COLLOCATED SAMPLERS

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CONTENTS

FIGURES

TABLES

CONVERSION FACTORS

Multiply	By	To obtain
milliliter (mL)	0.03381	ounce, fluid
liter (L)	1.057	quart
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
hectare (ha)	2.471	acre
milligram (mg)	35.27	ounce, avoirdupois
kilogram (kg)	2.205	pound

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 1.8 \times °C + 32$$

The following abbreviation also is used in this report:
µequiv. = microequivalents

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ABSTRACT

A collocated, wet-deposition sampler program has been operated since October 1988 to estimate the overall sampling precision of wet atmospheric deposition data collected at selected sites in the National Atmospheric Deposition Program and National Trends Network (NADP/NTN). Estimates of relative precision have been calculated that include variability in the data from the point of sample collection through storage of the data in the NADP/NTN data base.

Four sites representing diverse regional locations and precipitation regimes were selected and operated for each year of the study. At each site a collocated set of NADP/NTN wet deposition sampling equipment was installed following standard NADP/NTN protocol. Wet-deposition samples from collocated sites were processed by site operators using standard NADP/NTN procedures.

Laboratory analysis included determination of pH, specific conductance, and concentration of major cations and anions. Sampling precision was evaluated from the differences in the chemistry of the paired observations and precipitation depth from the collocated rain gages in units of median relative and absolute error for analyte concentration and deposition. Relative error for analytes whose concentrations typically approached laboratory method detection limits were greater than for analytes that did not typically approach detection limits. The median relative error for potassium and ammonium concentration and deposition exceeded 15 percent at most sites, while the median relative error for sulfate and nitrate concentration and deposition at all sites was less than 6 percent. The median absolute error for hydrogen ion ranged from 0.29 to 3.05 microequivalents per liter at the eight sites. Overall, collocated sampling error typically was five times that of laboratory error estimates for most analytes. Median absolute and relative error for precipitation depth, analyte concentration, and analyte deposition was greater for samples collected during the winter at two northern sites compared to other seasons. Bias, defined as the median of the signed collocated differences between sample pairs, generally accounted for less than 25 percent of the collocated variability in analyte concentration and deposition from weekly collocated precipitation samples.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was established in 1978 as a national monitoring network to investigate wet atmospheric deposition. The National Trends Network (NTN) was established in 1982 to introduce the NADP effort into areas not previously sampled and to provide long-term monitoring (10 years minimum) of the chemistry of wet deposition (Robertson and Wilson, 1985). Approximately 200 wet-deposition monitoring sites were in operation in 1991. The data collected within the NADP/NTN programs are used to monitor spatial and temporal trends in the chemical composition of wet deposition. Individual scientists and government agencies rely on NADP/NTN data to assess the effects of acid precipitation, determine trends in precipitation chemistry, and propose regulations to improve the quality of precipitation.

An NADP/NTN field site consists of an AeroChem Metrics[1] wet-dry precipitation sampler and a Belfort Universal recording rain gage. All site operators in the NADP/NTN use the same type of sample-collection instrument and sample-handling procedures (Bigelow, 1984; Bigelow and Dossett, 1988). Samples from each site are collected at 9 a.m. each Tuesday. All NADP/NTN samples are sent to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for chemical analyses (Peden, 1986). Because both networks use identical sampling and chemical-analysis protocols, the NADP and the NTN are considered as one program in this report.

In order to reduce scientific uncertainties regarding acid precipitation and its effect, the quality of NADP/NTN data must be rigorously defined. The quality of the NADP/NTN data is influenced by siting criteria (Bigelow, 1984); sample collection, handling, transportation and storage (Bigelow and Dossett, 1988); and laboratory analyses (Peden, 1986).

The goal of the U.S. Geological Survey (USGS) external quality-assurance programs is to describe the precision and bias of the chemical determinations of weekly NADP/NTN wet-deposition samples. To meet this goal, four separate programs are required to provide external quality assurance data on various aspects of the precipitation monitoring activities of the NADP/NTN. These four programs are the intersite comparison program, the blind-audit program, the interlaboratory comparison program and the collocated sampler program. A strong emphasis is placed on the quality assurance of onsite operations, as well as focusing on laboratory determinations.

The intersite comparison program is used to assess performance for onsite determination of pH and specific conductance. The blind-audit program provides an estimate of the analyte bias and precision that result from routine sample handling, shipping, and processing. The interlaboratory comparison program is used to determine if differences exist between the analytical results of laboratories that routinely measure constituents in precipitation samples. These three programs have been in operation since approximately 1978.

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[1] The use of trade or product names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The collocated sampler program was established in 1988 to estimate the overall precision of the precipitation-monitoring system. This estimate of precision includes variability in the data-collection system from the point of sample collection through storage of the data in the NADP/NTN data base. The ongoing collocated sampler program continues to increase the geographic and climatological coverage of the data on sampling precision for the NADP/NTN.

Purpose and Scope

This report describes the collocated sampler study, including the location of sites, installation of equipment, and visits to each site included in the study. In addition, estimates of intrasite precision are provided for sites included in the first 2 years of the study.

Previous Collocated Studies

Tang and others (1987) examined 4,000 daily wet-deposition samples collected from 5 rural sites in Ontario. The summer collection efficiency of 82.8 percent and the winter efficiency of 65.9 percent resulted in an annual collection efficiency of 75.3 percent when compared to a Canadian Meteorological Service rain gage. The lower relative collection efficiency was attributed partly to sensor lag of the AeroChem Metrics wet-dry precipitation sampler between precipitation initiation and sampling commencement. Reproducibility, calculated from collocated samples at the 5 Ontario sites exceeded 90 percent for sample depth, all major anions, hydrogen, ammonium, and magnesium concentration. Lower reproducibility for cations was attributed to cation concentrations near analytical detection limits.

As part of the Electric Power Research Institute Regional Experiment Precipitation program, Topol (1989) evaluated daily wet-deposition samples from collocated AeroChem wet-dry precipitation samplers at 5 to 21 sites in the Eastern United States. Precision was defined by the difference and ratio between collocated analyte pairs at the 50th and 85th percentile. The median ratio precision ranged from 4 percent for sulfate and nitrate to 8 percent for ammonium, 10 percent for hydrogen, and 13 percent for calcium. Bias, defined as the median of signed collocated differences, was less than 10 percent of precision values at nearly all sites. Laboratory precision, as determined by split samples from one of the collocated collectors, generally accounted for one-half of the overall monitoring error. Ratio precision estimates were lower in winter at both rain only and snow sampling sites for sample mass and most analytes. Lower concentration levels measured in winter may have accounted for lower analyte precision. The reason for reduced mass precision in winter at rain only sites was not determined. Fifteen percent of sampled events had collection efficiencies that differed by more than 20 percent. Analyte precision derived from this subset was generally reduced by a factor of 2 when compared to all samples.

Schroder and Malo (1984) conducted a replicate sampler study at Finley Farm, N.C., to evaluate daily and weekly sampler efficiencies for the AeroChem Metrics wet-dry precipitation sampler versus weighing rain gages. Average AeroChem collection efficiency was 97 percent for weekly rain-sampling periods compared to the weighing gage. Seasonality and precipitation volume were not shown to be significant variables in determining sampler collection efficiency.

In an examination of several collocated sampler studies, Bigelow (1986) noted that precision estimates calculated by a median ratio or relative percent difference method yielded numerically lower precision values than traditional calculations that used a comparison of annual or seasonal averages from each collector.

Acknowledgments

This study would not have been possible without the cooperation of the site operators and supervisors at each of the past and present collocated NADP/NTN sites.

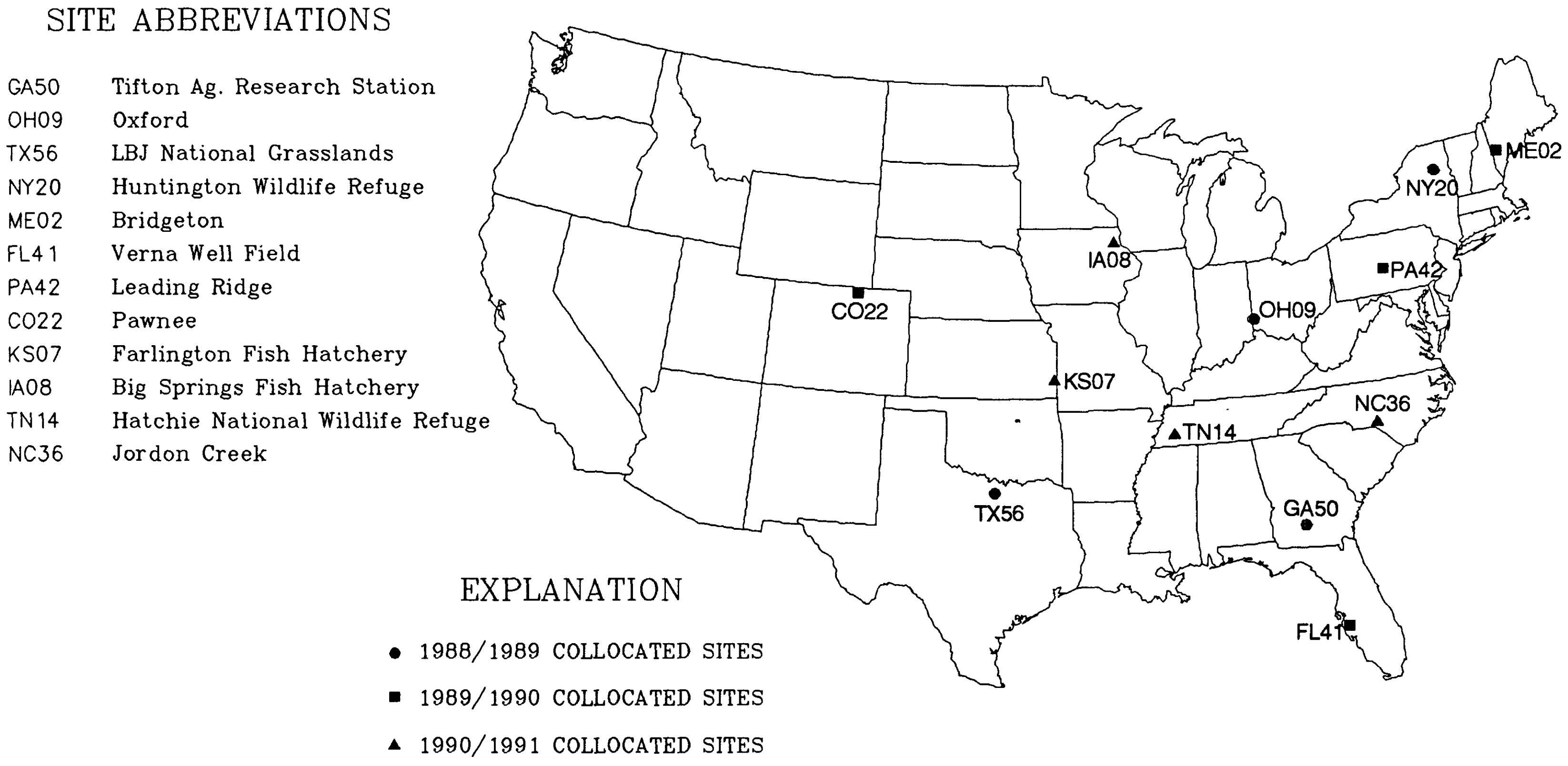
SITE SELECTION, INSTALLATION, AND OPERATION

Four sites that met several criteria were selected for each year of the collocated sampler study. A distribution of sites among diverse regional locations and among a range of precipitation regimes was needed. Only those sites with stable operational histories were considered in order to minimize data loss due to changes in personnel. Lack of room for collocated equipment was a common reason for eliminating several otherwise suitable fenced sites from consideration. The locations of sites selected to date for the collocated study to date are shown in figure 1. Data sets from the four sites operated during 1990-1991 are not yet complete and are not considered in this analysis. A brief summary of information available for each site in the NADP/NTN includes photographs and maps of the site, identification of operating and sponsoring organizations, characteristics of surroundings, and identification of original equipment at the site (Robertson and Wojciechowski, 1986).

NADP/NTN guidelines for site selection and installation (Bigelow, 1984) were used in the establishment of each collocated site. Equipment was shipped by the USGS to each site and site supervisors or operators completed the installation of the equipment. Samples from each pair of collectors were processed by the site operator by using standard NADP/NTN procedures (Bigelow and Dossett, 1988). Onsite pH and specific-conductance measurements were not made on the samples from the newly installed collocated samplers; however, a 20-mL aliquot was removed from samples of 70 mL or larger in order to provide equivalent treatments to both samples from the collocated site. All samples were analyzed by the CAL.

SITE VISITS

All sites selected for the collocated sampler study were inspected by USGS personnel. The four 1989 sites were inspected in the spring of 1989 after several months of sampling. The 1990 and 1991 sites were inspected in August or September after equipment installation and before collection of the first sample.



GA50	Tifton Ag. Research Station
OH09	Oxford
TX56	LBJ National Grasslands
NY20	Huntington Wildlife Refuge
ME02	Bridgeton
FL41	Verna Well Field
PA42	Leading Ridge
CO22	Pawnee
KS07	Farlington Fish Hatchery
IA08	Big Springs Fish Hatchery
TN14	Hatchie National Wildlife Refuge
NC36	Jordon Creek

Figure 1.--Location of National Atmospheric Deposition Program/National Trends Network sites with collocated samplers

At each site the original and the collocated NADP/NTN equipment was inspected to assure that it was installed correctly and functioning properly. The sensor temperature of the AeroChem Metrics wet-dry precipitation sampler was measured at three points prior to and 5 minutes following activation. The resistance at which the sensor activated lid openings and closing was measured with a Beckman Heliopot potentiometer, fixed resistors, and a Fluke Multimeter. The lid drop distance was measured with the wet-deposition bucket in place and again with the bucket removed to estimate how evenly and securely the lid covered the bucket. The sensor gap between the grid and plate was measured at two locations on each sensor by using feeler gages.

The calibration of the Belfort recording precipitation gages was checked with standard weights through the entire instrument range and adjusted if necessary (Belfort Instrument Company, 1986). Event recorder function was checked visually and by voltage measurements at the recorder terminals while activating the wet-dry collector. Distances between all site equipment were determined, photographs were taken from eight directions, and site maps were sketched. Faulty equipment was replaced during the visits or replacement parts were ordered immediately. The site operators or supervisors made all installations of replacement parts that were provided following the inspection.

DATA ANALYSIS

The Illinois State Water Survey, CAL has provided qualified data for October 1988-October 1990. The CAL assigned each NADP/NTN sample a lab type code that indicates the condition of the sample as it arrived at the CAL. For this data analysis, only data from normal wet-deposition samples with volume greater than 35 mL (lab type "W") that did not require dilution were used in the statistical summaries. Median sample concentrations in weekly samples from the eight sites are presented in table 1.

Several short-term equipment malfunctions affected the samplers during the study. Problems such as total site power outages, which impacted the original and collocated equipment in the same manner, were not grounds for exclusion of the sample data from this report. In addition, undocumented, intermittent malfunctions of the original or collocated sampling equipment undoubtedly occurred. For example, a few collocated samples differed in volume by more than 2,000 mL for the weekly sampling period. Care was taken to select statistics that were meaningful in describing overall sampling precision and were not overly sensitive to a small number of extreme outliers.

Annual summaries of NADP/NTN data describe precipitation chemistry in units of concentration and deposition for ionic constituents (National Atmospheric Deposition Program, 1990). Precision estimates for both concentration and deposition of ionic constituents are included in this report. The weekly precipitation depth associated with each Belfort recording rain gage was used in this report to calculate deposition values. This approach accounts for the variability due to differences in rain gage collection efficiency to be included in the precision estimates for deposition. Variability in sample volume between the collocated AeroChem wet-dry precipitation samplers is not explicitly addressed by this approach.

Table 1.--*Median analyte concentrations and volume in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages*

[All units in milligrams per liter except hydrogen, in microequivalents per liter; specific conductance (cond.), in microsiemens per centimeter at 25 °C; sample volume, in milliliters; and precipitation depth (Precip. depth), in centimeters. See figure 1 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	0.099	0.154	0.351	0.093	0.045	0.139	0.135	0.189
Magnesium	.045	.026	.043	.017	.015	.058	.025	.028
Sodium	.225	.064	.176	.052	.078	.405	.059	.084
Potassium	.038	.018	.050	.014	.018	.027	.022	.036
Ammonium	.18	.39	.31	.23	.23	.18	.38	.54
Chloride	.45	.16	.26	.12	.17	.72	.21	.15
Nitrate	.83	1.63	1.37	1.95	1.38	.69	2.58	1.73
Sulfate	1.16	2.53	1.35	1.89	1.82	.93	3.07	.99
Hydrogen	14.59	44.16	2.98	36.78	42.70	8.81	66.10	.93
Specific cond.	12.65	25.00	12.20	21.70	22.10	11.35	37.15	9.90
Sample volume	1,157.7	1,299.2	1,365.8	998.2	1,147.0	1,791.0	883.0	495.1
Precip. depth	1.94	2.06	2.08	1.68	1.77	2.27	1.73	.80

Precision estimates for each site are calculated from the relative and absolute differences between the pairs of collocated samples and are expressed as median relative and median absolute error for a given site and analyte. The equations used to estimate median relative and absolute error from collocated data are:

$$\text{Median relative error (in percent)} = M\left|\frac{C_1 - C_2}{(C_1 + C_2)/2}\right| \cdot 100$$

$$\text{Median absolute error (in mg/L or kg/ha)} = M|C_1 - C_2|$$

where

M = median of all paired differences;

C_1 = Sample concentration (mg/L) from the original precipitation sampler, or deposition (kg/ha) from the original precipitation sampler and rain gage;

C_2 = Sample concentration (mg/L) from the collocated precipitation sampler, or deposition (kg/ha) from the collocated precipitation sampler and rain gage.

Precision estimates defined here by the median of the unsigned absolute or relative percent difference are fairly insensitive to a small number of extreme values. For sample pairs with low concentration of ionic constituents, the relative percent error can be very large, although the absolute difference between the samples is small. The median number of valid sample pairs per site was 45 and ranged from a high of 51 at NY20 to a low of 29 at CO22. When one or both of the paired measurements for a given analyte were reported as below method detection limits, results from that date were not used in the calculation of precision for that site.

Precision Estimates

Precision estimates of precipitation chemical concentration and deposition for the eight sites are presented in tables 2 and 3. Nitrate and sulfate concentration had the smallest relative error, ranging from 1.8 percent to 5.9 percent among the sites. Typical nitrate and sulfate concentrations were much greater than method detection limits. Relative error for potassium and ammonium concentration and deposition exceeded 15 percent at most sites. The larger relative error for potassium and ammonium compared to other analytes might be attributable to concentrations that were near method detection limits for many samples. The greatest variation in precision between any two of the eight sites occurred for hydrogen-ion deposition, with median relative error ranging from 4.6 percent at PA42 to 37.6 percent at CO22 (table 3). The large difference in precision estimates for hydrogen at those two sites can be accounted for by the difference in median concentration. Median hydrogen-ion concentration at PA42 was 70 times greater than that of CO22. The smallest variation in median relative error was noted for sulfate concentration, which ranged from 1.9 percent to 4.8 percent among sites (table 2). The analyte concentration and volume differences between samples from original and collocated samplers and precipitation depth differences from original and collocated rain gages are presented as box plots in figures 5 to 16 in the appendix.

Median relative error calculated for weekly analyte deposition at the eight sites incorporates variability due to differences in sample depth between the original and collocated Belfort recording rain gages. Although not consistent among sites or analytes, median relative errors typically were 2 to 5 percentage points higher when calculated using deposition data rather than concentration data.

Precision and Concentration

Scatter plots of relative percent error versus average concentration are provided in figures 2 through 4 for selected sites and analytes. Assuming that random contamination is independent of sample concentration, an increase in relative error at lower concentrations would be expected. At lower concentrations, near the method detection limit, relative error increases sharply for most analytes examined in this report. This trend seems more pronounced for major cation species than for anions. For example, the three sample pairs that differed by more than 100 percent at site ME02 for calcium were low-concentration samples. Relative error for sulfate and nitrate appear to have the least concentration dependence, although extreme outliers for these analytes cluster in the lower range of concentrations. A small number of outliers, typically one order of magnitude greater than the median collocated error, occur for virtually every site and analyte examined.

Table 2.--*Median relative error for analyte concentrations and sample volume in weekly samples from collocated wet-dry precipitation collectors*

[All data expressed in percent; cond., conductance. See figure 1 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	13.1	10.8	7.6	20.4	25.9	10.5	12.4	9.1
Magnesium	9.1	9.5	12.5	22.2	18.2	6.3	13.3	15.4
Sodium	4.7	11.5	6.6	20.2	13.7	4.5	14.4	22.3
Potassium	19.3	19.2	26.1	43.5	28.5	21.0	46.9	29.6
Ammonium	16.1	9.5	21.1	21.3	17.1	22.2	9.8	19.0
Chloride	2.4	6.5	6.9	13.3	11.7	6.1	9.2	12.2
Nitrate	3.2	3.3	3.5	5.9	2.8	2.8	1.8	4.5
Sulfate	2.3	3.5	3.6	3.5	3.1	3.4	1.9	4.8
Hydrogen	16.1	4.6	28.6	13.8	4.6	11.5	3.5	34.2
Specific cond.	3.1	5.8	7.0	6.3	3.2	4.9	2.2	5.2
Sample volume	1.2	2.0	1.5	3.4	1.1	1.5	1.5	4.2

Table 3.--*Median relative error for analyte deposition in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages*

[All data expressed in percent; Precip., precipitation. See figure 1 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	20.8	14.0	8.0	21.6	28.7	10.6	14.8	15.8
Magnesium	12.8	8.7	8.5	19.0	17.1	6.6	12.8	19.2
Sodium	7.2	13.5	6.7	25.8	16.6	5.1	14.6	24.0
Potassium	23.1	23.3	26.1	38.2	29.4	24.6	48.3	21.4
Ammonium	20.3	10.1	22.2	20.5	19.5	21.2	9.9	33.9
Chloride	7.5	7.4	11.4	20.7	14.9	4.0	9.9	12.5
Nitrate	5.8	4.9	4.9	10.7	8.7	3.8	3.9	12.2
Sulfate	6.3	4.2	4.2	11.0	8.2	4.5	2.9	14.6
Hydrogen	13.6	7.4	27.2	13.2	9.2	13.7	4.6	37.6
Precip. depth	4.8	2.2	1.1	8.0	2.8	3.3	1.2	5.9

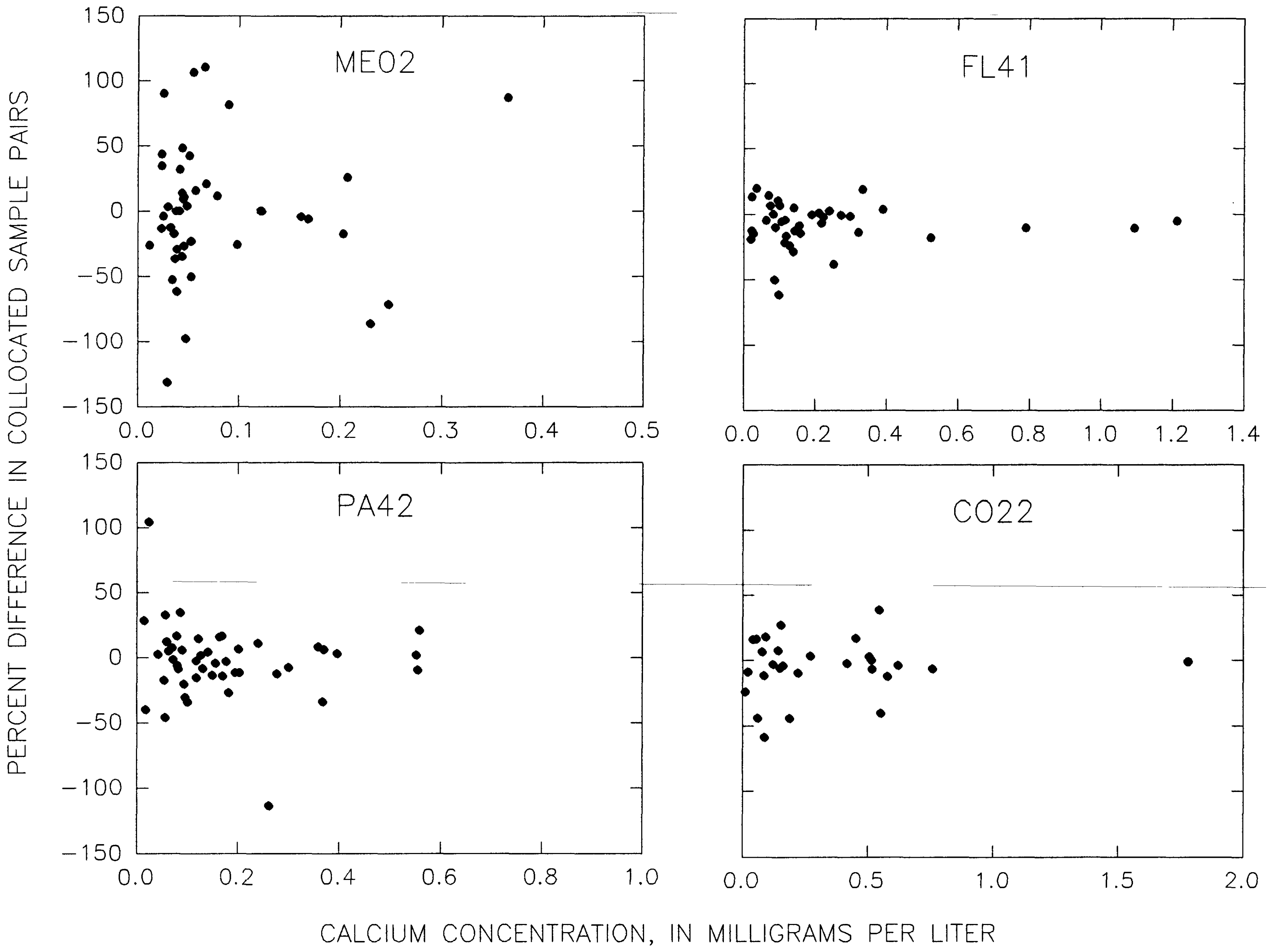


Figure 2.--Comparison of calcium relative percent error and the average calcium concentration at four sites with collocated samplers. [See figure 1 for an explanation of site abbreviations.]

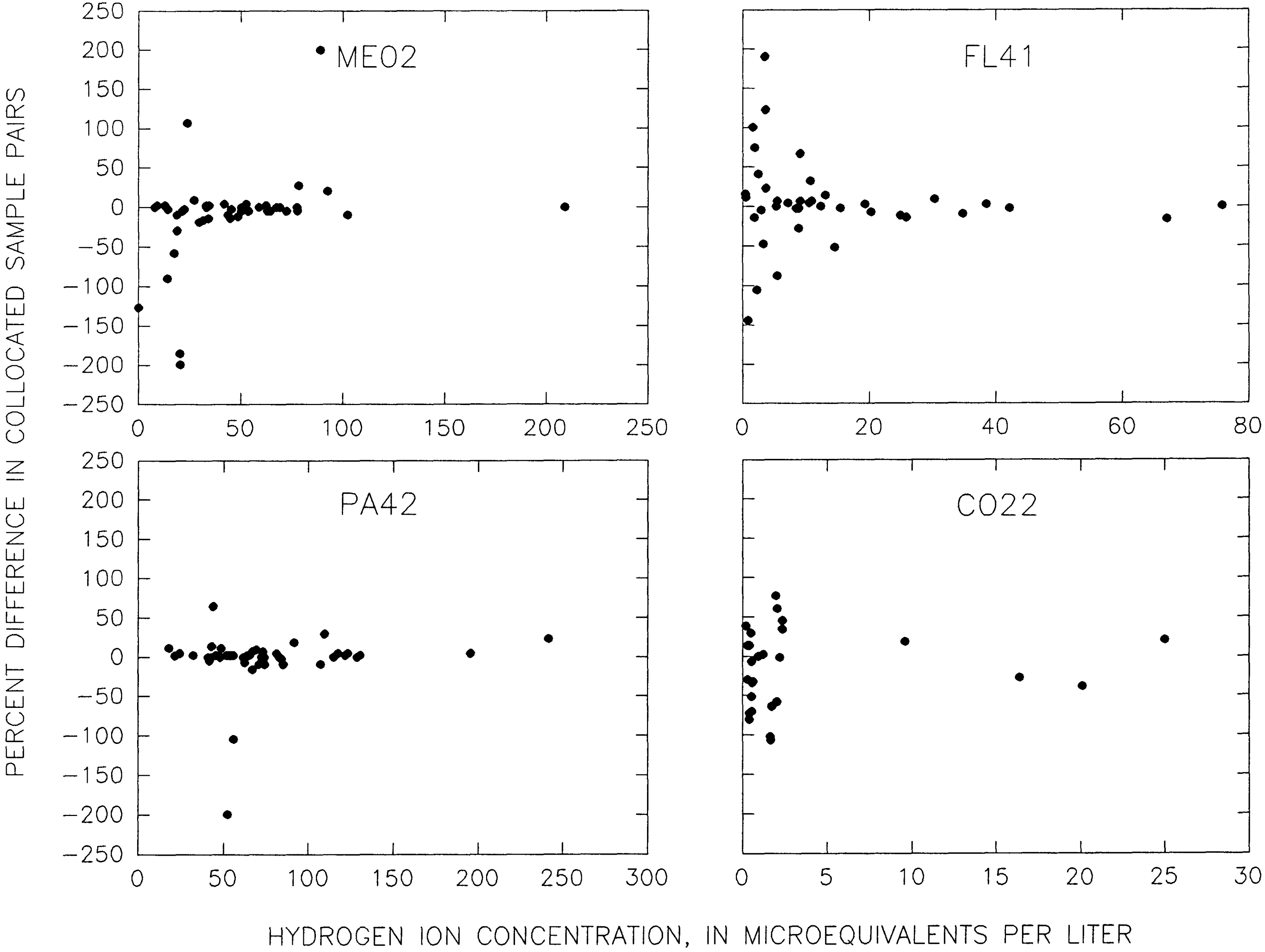


Figure 3.--Comparison of hydrogen relative percent error and the average hydrogen concentration at four sites with collocated samplers. [See figure 1 for an explanation of site abbreviations.]

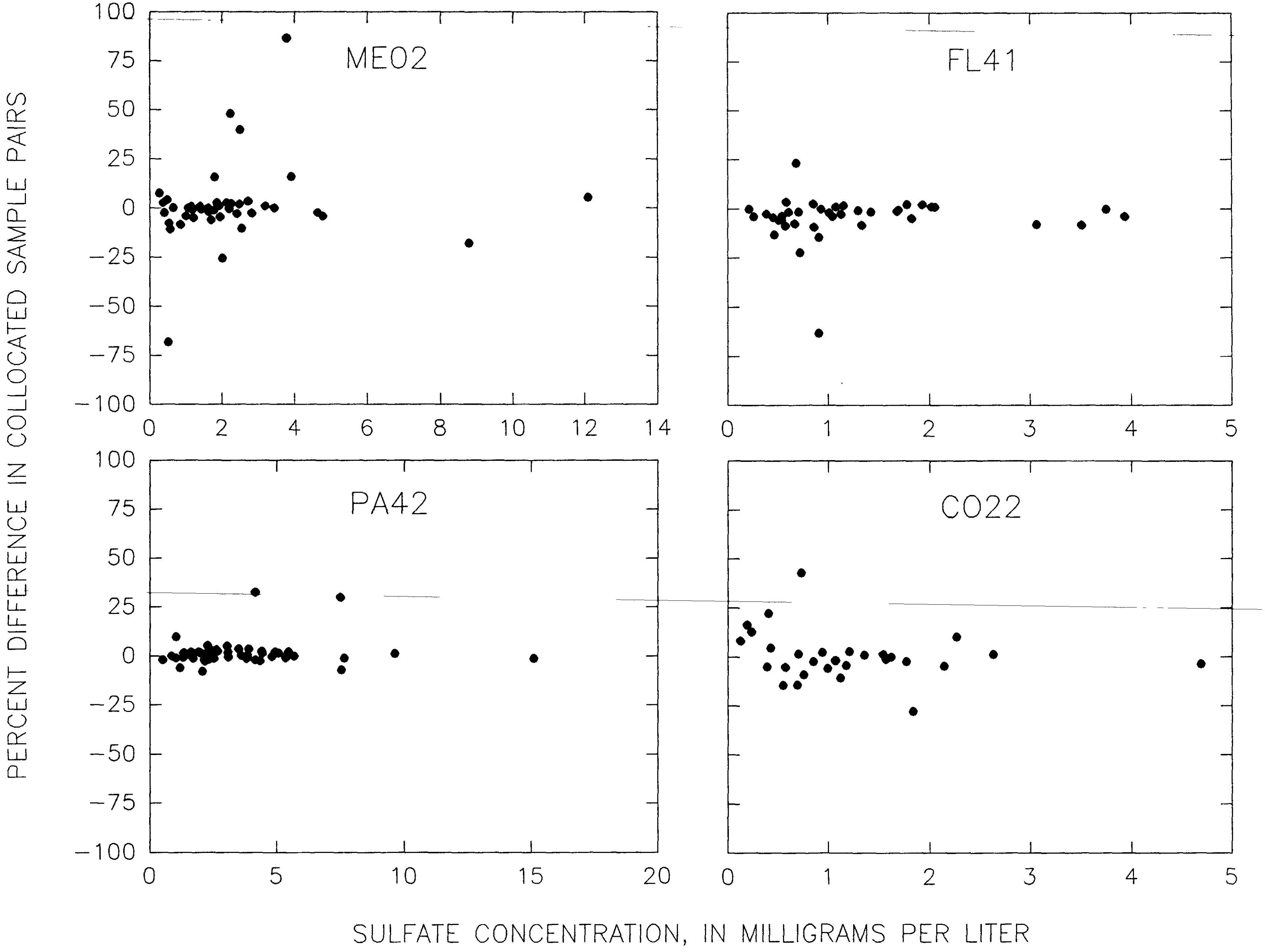


Figure 4.--Comparison of sulfate relative percent error and the average sulfate concentration at four sites with collocated samplers. [See figure 1 for an explanation of site abbreviations.]

Precision and Seasonality

Collocated data from two northern sites, NY20 and ME02, were selected to compare the precision of snow-dominated sampling to that of rain. Decreased precision for snow sampling compared to rain has been widely reported in previous collocated studies (de Pena and others, 1980; Topol, 1989). Decreased precision was attributed to diminished and more variable collection efficiency by the AeroChem Metrics wet-dry precipitation sampler during a snow event than during a rain event.

Precision estimates derived from collocated samples collected during the winter (defined as the period November 29-February 28, 1988 and 1989) are compared in table 4 to estimates derived from samples collected during the entire year. Median relative error in collocated samples was 1.5 to 2 times greater for most analytes when calculated from snow-dominated sample data. Winter season collocated median error calculated for precipitation depth was 1.4 and 2.2 times greater at the New York and Maine sites, respectively, when compared to annual data. Owing to the limited number of sites and data pairs available to compare snow-dominated to rain-dominated sampling, these estimates of precision should be regarded as preliminary.

Table 4.--*Median relative error for analyte concentrations, sample volume, depositions, and precipitation depth in weekly samples for winter and annual data from collocated wet-dry precipitation collectors and rain gages*

[All data expressed in percent. --, no data; cond., conductance; Precip., precipitation. See figure 1 for an explanation of site abbreviations]

Analytes	Sampling sites							
	NY20 WINTER	NY20 ANNUAL	ME02 WINTER	ME02 ANNUAL	NY20 WINTER	NY20 ANNUAL	ME02 WINTER	ME02 ANNUAL
	CONCENTRATION				DEPOSITION			
Calcium	29.6	20.4	31.9	25.9	26.9	21.6	42.2	28.7
Magnesium	33.7	22.2	34.5	18.2	27.7	19.0	38.0	17.1
Sodium	21.6	20.2	35.8	13.7	22.4	25.8	31.1	16.6
Potassium	69.7	43.5	28.6	28.5	60.0	38.2	30.3	29.4
Ammonium	35.6	21.3	8.0	17.1	25.7	20.5	14.1	19.5
Chloride	15.5	13.3	12.9	11.7	20.2	20.7	26.0	14.9
Nitrate	9.7	5.9	8.8	2.8	22.1	10.7	20.7	8.7
Sulfate	17.9	3.5	9.3	3.1	22.1	11.0	28.2	8.2
Hydrogen	20.6	13.8	10.4	4.6	19.0	13.2	29.1	9.2
Specific cond.	18.0	6.3	13.6	3.2	--	--	--	--
Sample volume	7.7	3.4	13.3	1.1	--	--	--	--
Precip. depth	--	--	--	--	10.8	8.0	6.1	2.8

Collocated and Analytical Precision

Collocated analyte precision estimates are compared in table 5 to analytical precision estimates calculated in the same manner from 104 replicate natural precipitation samples submitted to the CAL in 1989 and 1990 as part of an interlaboratory comparison program. Aliquots of natural, weekly, wet-deposition samples with volumes greater than 750 mL are used in the USGS interlaboratory comparison programs. The natural interlaboratory samples had slightly lower specific conductance and median concentrations of analytes when compared to all NADP/NTN network samples analyzed at the CAL. This program is described in detail by Willoughby and others (1991). Laboratory random error, as calculated from replicate samples submitted to the CAL for analysis, is estimated typically to account for one-fifth of the overall collocated sampling error, although differences obviously occur at different sites and for various analytes. Estimated laboratory error typically exceeded 25 percent of the median collocated sampling error for chloride ion.

Laboratory error is calculated in this report from a random group of replicate samples selected from the universe of NADP/NTN wet deposition samples submitted to the CAL for analysis. This measure of laboratory error is not comparable on a direct basis to overall sampling error for an individual collocated site owing to differences in analyte chemistry between the two populations. For example, one might infer from table 5 that laboratory error in the determination of hydrogen ion accounts for 100 percent of the overall sampling error at site CO22. This type of specific partitioning of error would only be valid if the laboratory error term was calculated from a number of replicate samples collected at site CO22.

Table 5.--*Median absolute error for analyte concentrations from weekly collocated wet-dry precipitation samples and replicate natural samples*

[All units in milligrams per liter except: hydrogen in microequivalents per liter; and specific conductance in microsiemens per centimeter at 25 °C. CAL, Central Analytical Laboratory Illinois State Water Survey; cond., conductance. See figure 1 for an explanation of site abbreviations.]

	Sampling site								
Analyte	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22	CAL
Calcium	0.009	0.018	0.024	0.018	0.012	0.010	0.019	0.016	>0.001
Magnesium	.004	.003	.003	.003	.003	.004	.003	.004	.001
Sodium	.012	.007	.008	.012	.012	.016	.010	.015	.002
Potassium	.005	.004	.014	.005	.004	.005	.010	.009	.001
Ammonium	.03	.03	.07	.04	.03	.04	.03	.08	>.01
Chloride	.01	.01	.02	.01	.02	.02	.02	.02	>.01
Nitrate	.02	.06	.04	.13	.05	.02	.04	.06	.01
Sulfate	.03	.11	.04	.08	.05	.02	.06	.03	.01
Hydrogen	1.85	3.05	.49	2.86	2.45	1.03	2.01	.29	.31
Specific cond.	.50	1.50	.65	1.40	.70	.60	.70	.50	.20

Bias in Collocated Measurements

Bias was evaluated for each site and analyte using the median signed difference between collocated sample concentrations and is presented in table 6. Bias estimates for sample volume from the AeroChem precipitation collectors and precipitation depth from the Belfort recording rain gages also are provided. Because the collocated paired samples were shipped from the sites weekly to the same laboratory at the same time, the authors attribute bias in the data set pairs to systematic differences in: 1) sampler response, 2) sample collection, and 3) sample handling prior to shipment. Bias for most analytes accounted for less than 20 percent of the overall relative error in collocated measurements. The bias at site GA50 (fig. 1) was zero percent for 7 of the 10 analytes examined and exceeded 2 percent only for calcium. The median signed difference in sample volume collected from the samplers at GA50 was +0.2 percent. With the exception of hydrogen ion, the bias in every analyte examined at site FL41 (fig. 1) exceeded -2.5 percent and exceeded -5.0 percent for calcium, potassium, ammonium, and chloride. The bias in collected sample volume at FL41 was -1.2 percent. The data suggest a relation between collected sample volume at collocated sites and bias in analyte concentration. Further study is needed to confirm this relation.

Table 6.--*Bias for analyte concentrations and sample volume in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages*

[All data expressed in percent; cond., conductance; Precip., precipitation. See figure 1 for an explanation of site abbreviations.]

Analyte	Sampling site							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	2.1	-10.3	5.4	-6.2	0.0	-5.6	0.7	-3.3
Magnesium	0.0	-4.7	4.7	-6.9	0.0	-4.2	0.0	0.0
Sodium	0.0	0.0	3.3	-4.7	6.3	-4.4	8.3	0.0
Potassium	0.0	-10.5	0.0	-34.8	0.0	-6.9	23.9	1.8
Ammonium	0.0	-2.8	-6.3	-5.4	6.4	-8.7	0.0	-2.1
Chloride	0.0	0.0	2.2	0.0	5.2	-5.5	7.4	0.0
Nitrate	0.0	-2.9	3.5	-2.9	0.0	-2.7	0.9	-2.4
Sulfate	-0.3	-2.3	2.0	-1.2	0.0	-2.6	0.5	-1.2
Hydrogen	0.0	-2.3	0.0	0.0	-2.3	0.0	2.3	-27.5
Specific cond.	1.0	-3.5	5.9	-1.6	-0.6	-2.6	1.0	2.0
Sample volume	0.2	-1.9	0.8	-1.3	-0.1	-1.2	0.6	-3.3
Precip. depth	-3.9	0.0	0.0	2.4	0.6	1.8	0.0	-2.0

SUMMARY

An ongoing collocated sampler program was established to estimate the overall variability of chemical measurements of wet-deposition data collected for the NADP/NTN. The estimates of precision include all variability in the data-collection system, from the point of sample collection through storage in the NADP/NTN data base. Weekly wet-deposition samples and precipitation measurements from collocated NADP/NTN sites were compared.

Sites were selected to cover a wide range of geographic and climatological conditions and were established and operated using standard NADP/NTN protocols. Collocated sites were visited by U.S. Geological Survey personnel to assure that equipment was functioning properly and met NADP/NTN siting protocol. All samples were analyzed by the Illinois State Water Survey, Central Analytical Laboratory (CAL). Only wet deposition samples that did not require dilution (volume greater than 35 mL) at the CAL were used in the statistical analysis. Estimates of precision were calculated in units of median relative difference and in terms of median absolute difference for both concentration and deposition of ionic constituents of wet deposition.

The median relative error for sulfate and nitrate was typically less than the median relative error calculated for all other analytes examined. Relative error typically was greatest for potassium and ammonium ion, with median relative error exceeding 15 percent at most sites. At lower concentrations, relative error increased for most analytes. Relative error for analytes whose concentrations typically approached laboratory method detection limits were greater than for analytes that did not typically approach detection limits. Median relative error estimated from samples collected during winter at two northern sites was greater than the relative error calculated from all samples at the same two sites. Laboratory error is estimated to account for typically one-fifth of the overall collocated sampling error on the basis of data from replicate natural samples analyzed at the CAL. Bias in collocated measurements typically accounted for less than 25 percent of the overall error in collocated measurements. Calculation of regional or larger scale precision estimates, the objective of the collocated sampler program, will require collocated sampling data from many additional network sites.

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APPENDIX

Box plots of chemical, volume, and precipitation depth differences between original and collocated wet-deposition samples and rain gage measurements.

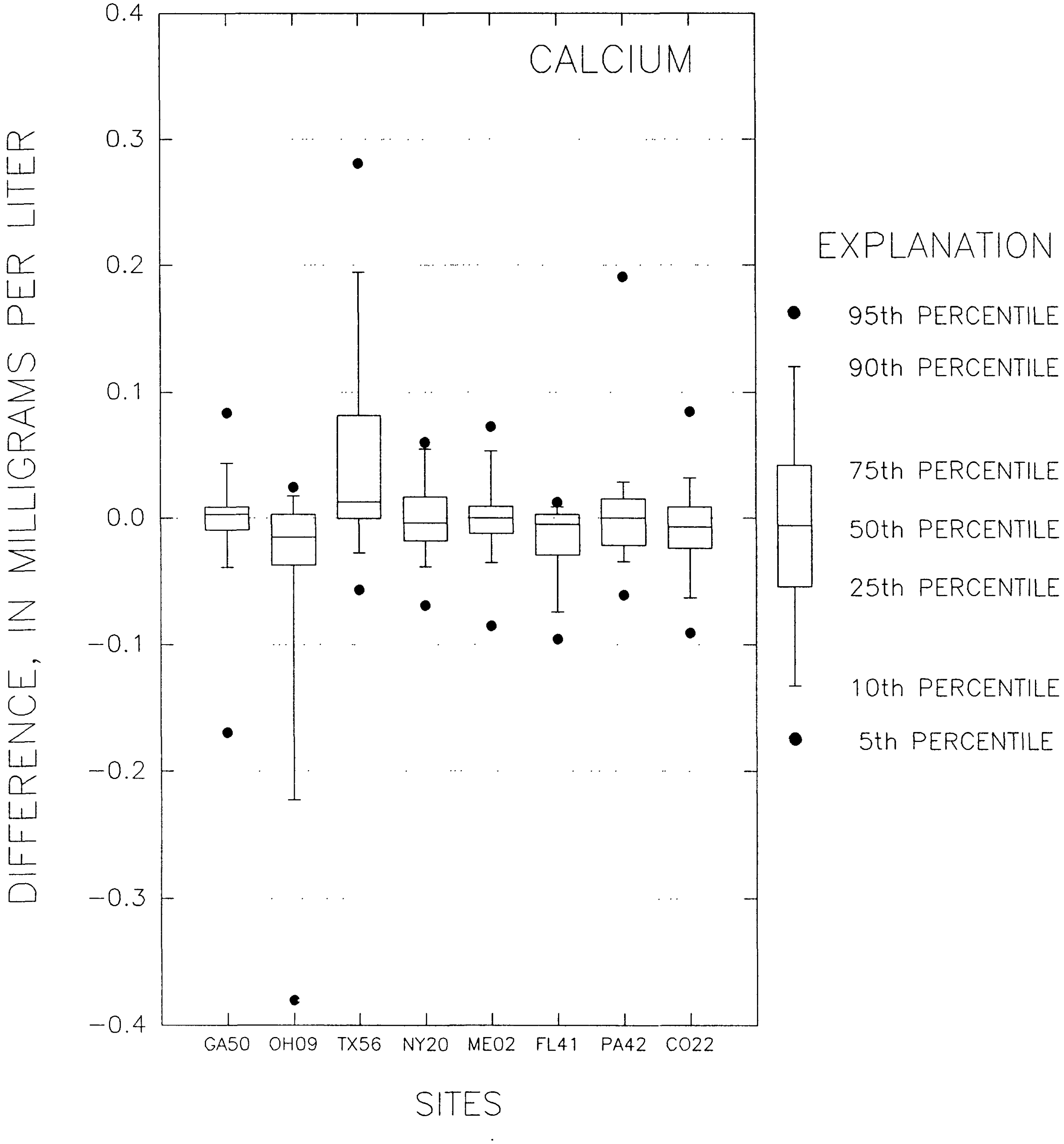

Figure 5.--Difference in calcium concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

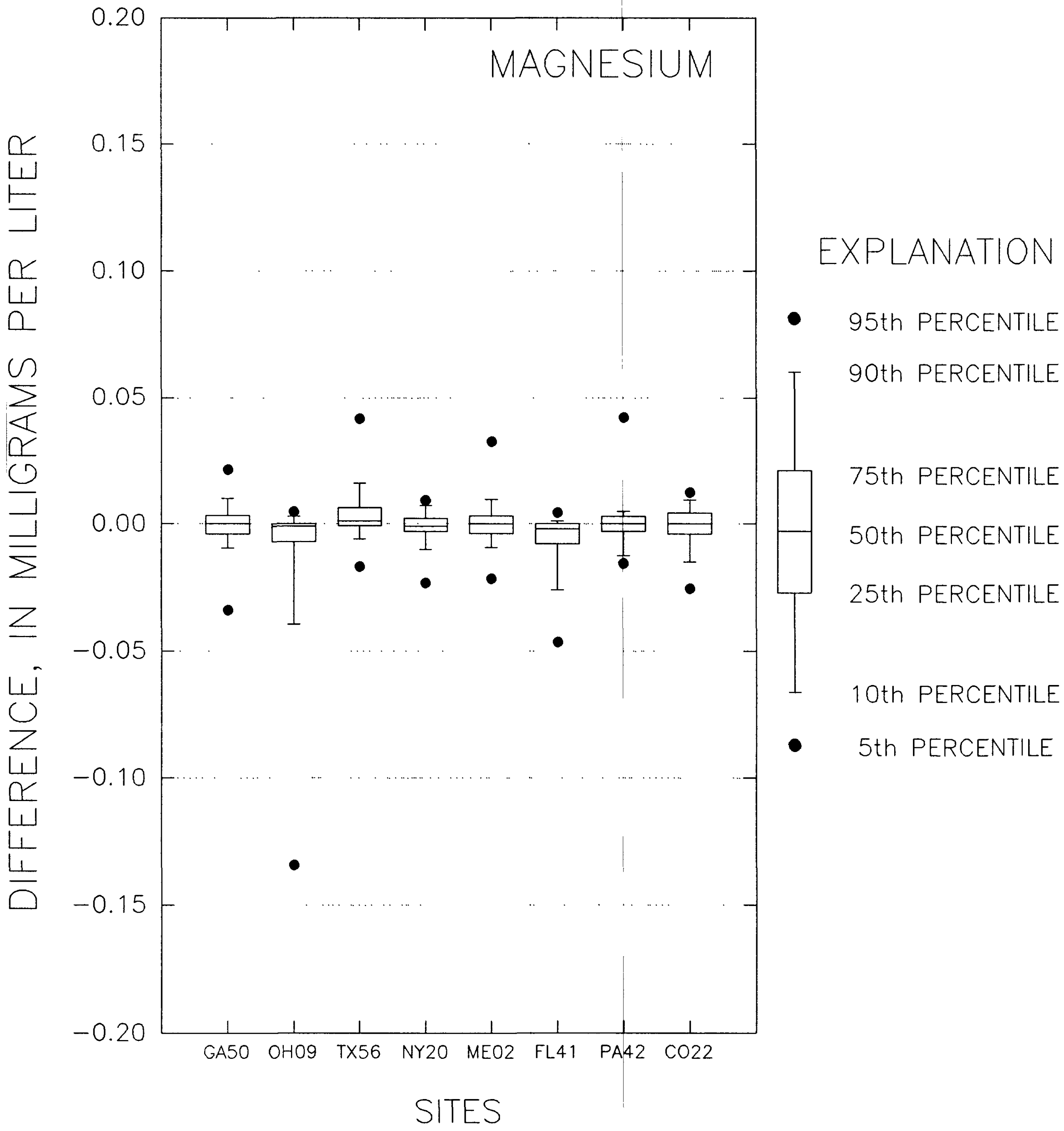

Figure 6.--Difference in magnesium concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

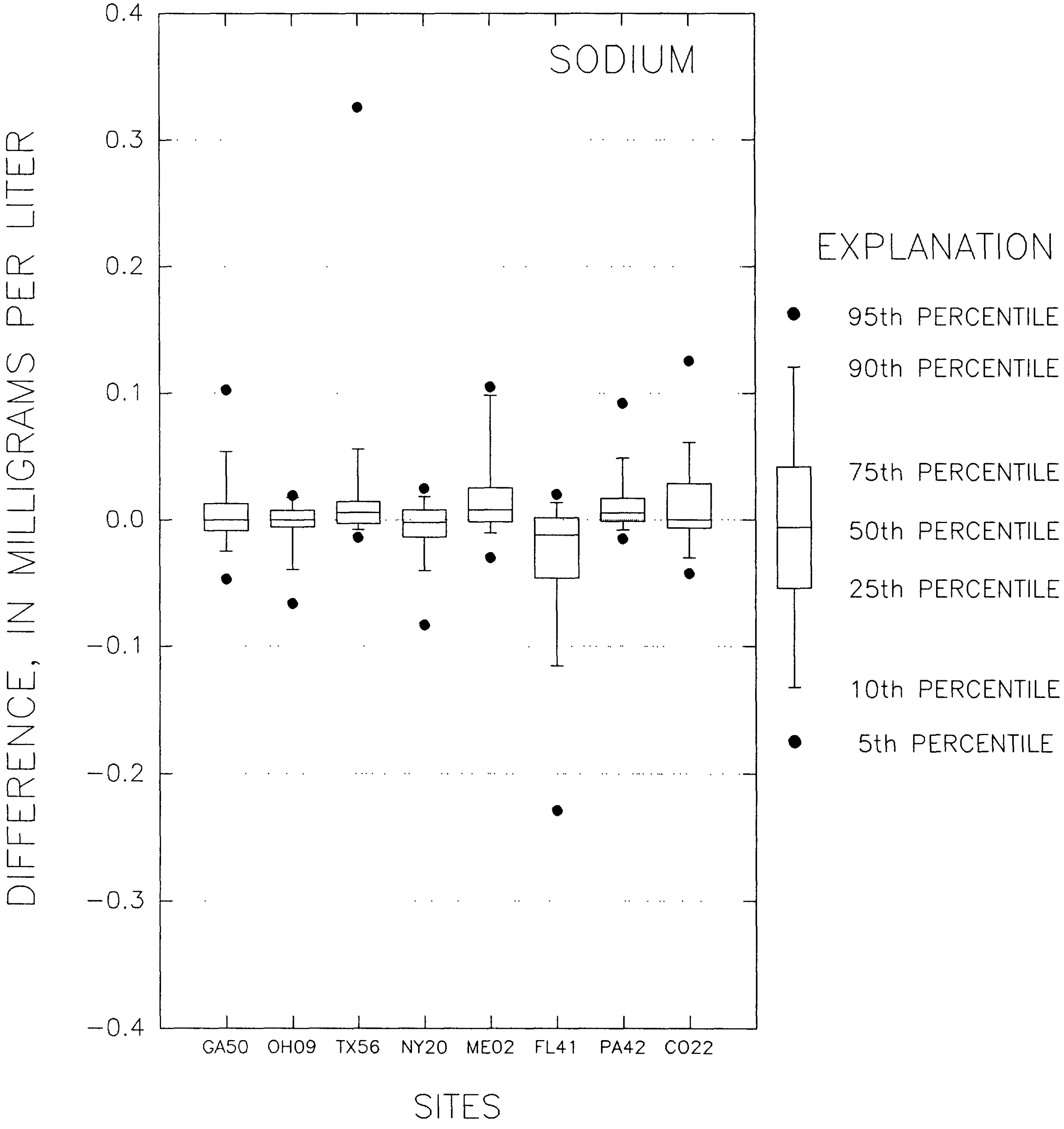

Figure 7.--Difference in sodium concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

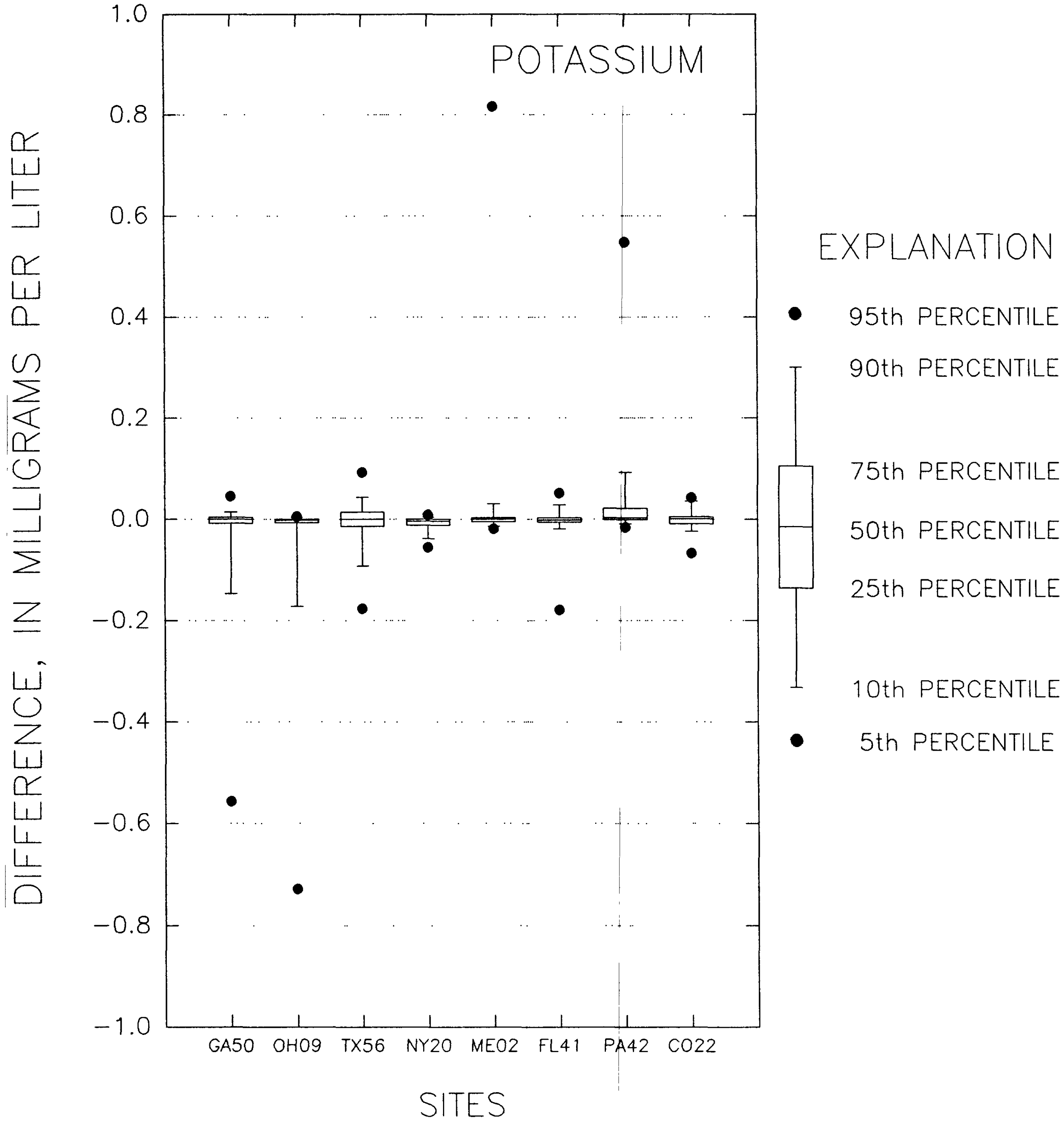

Figure 8.--Difference in potassium concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

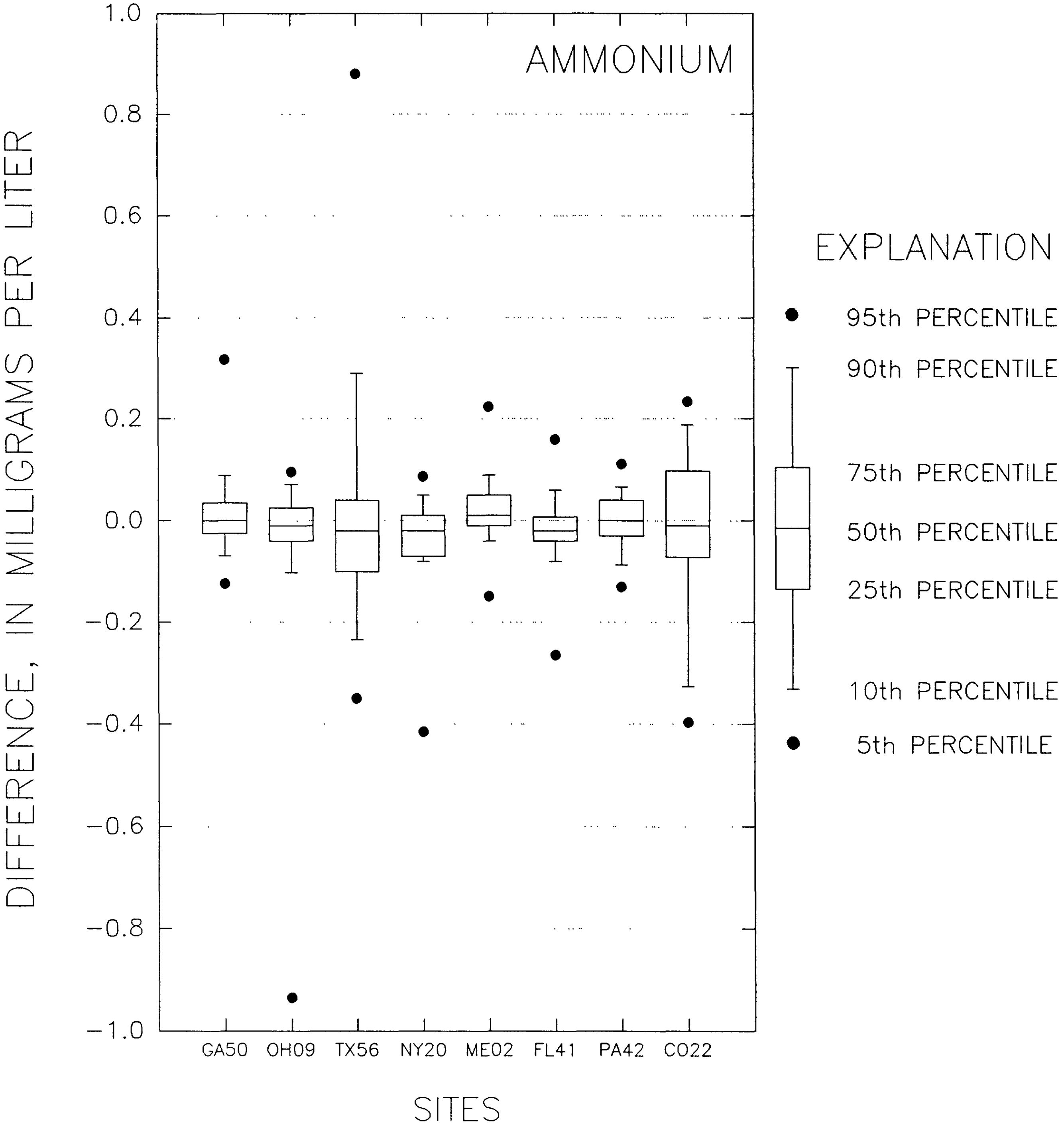

Figure 9.--Difference in ammonium concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

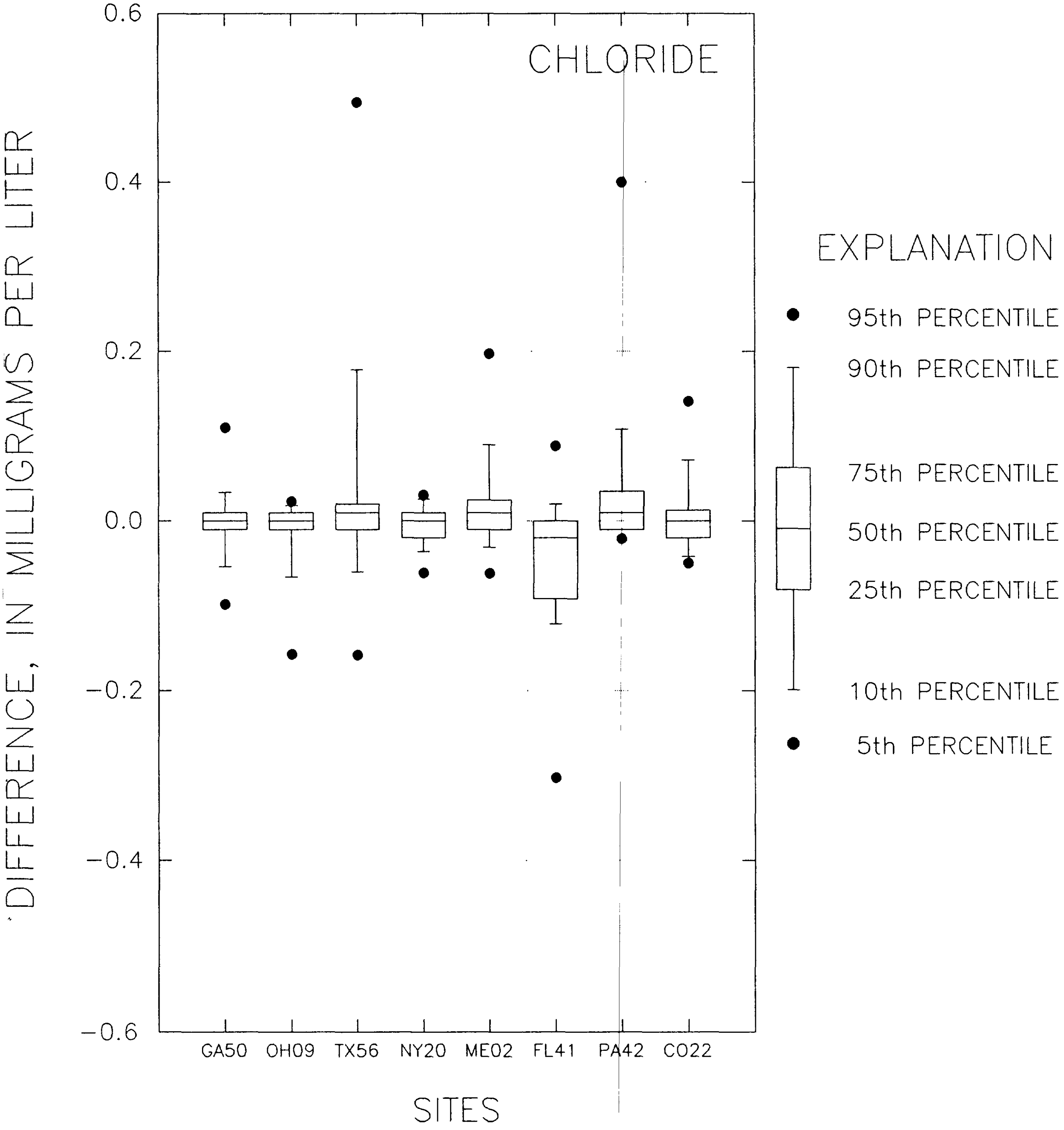

Figure 10.--Difference in chloride concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

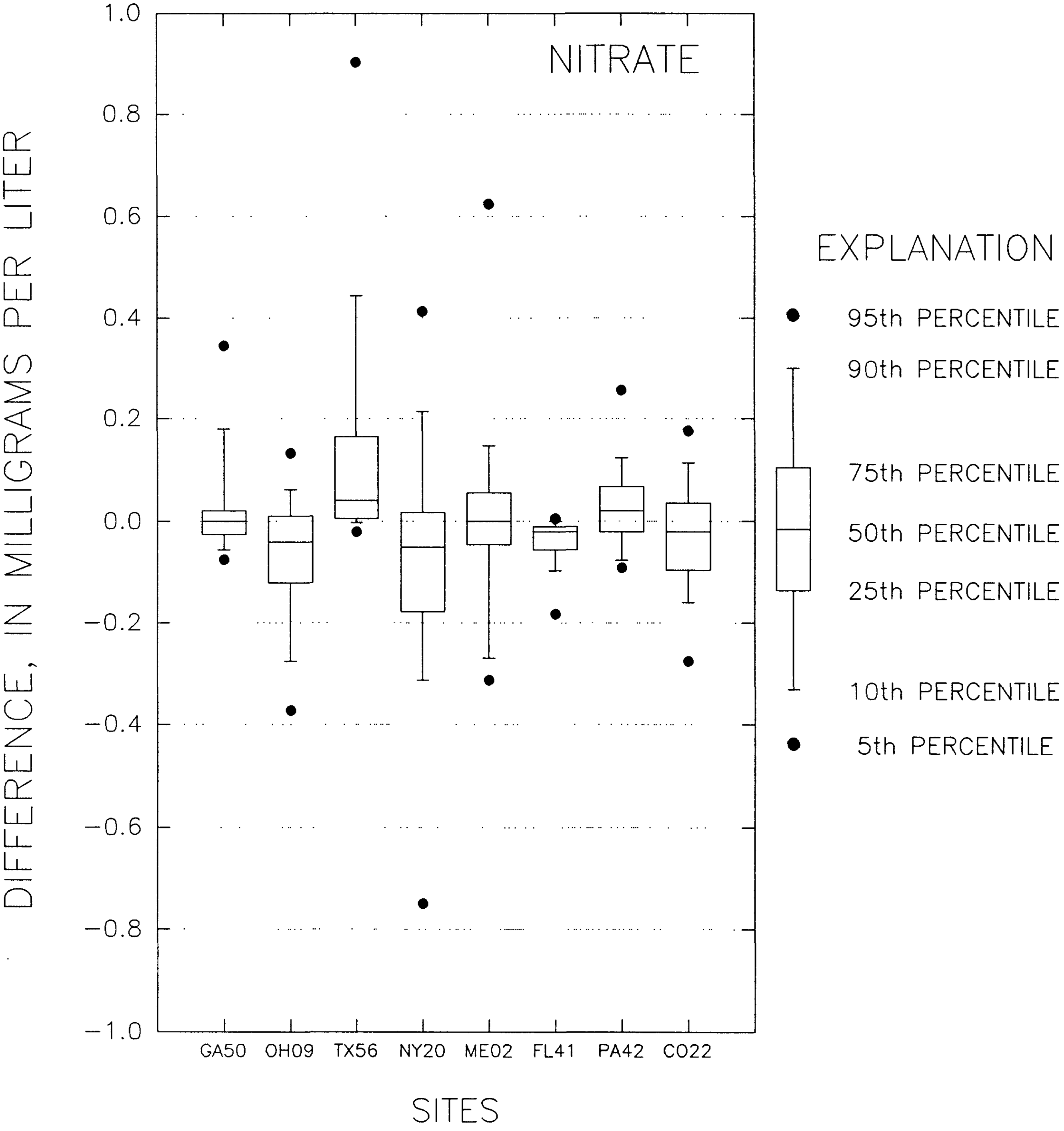

Figure 11.--Difference in nitrate concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

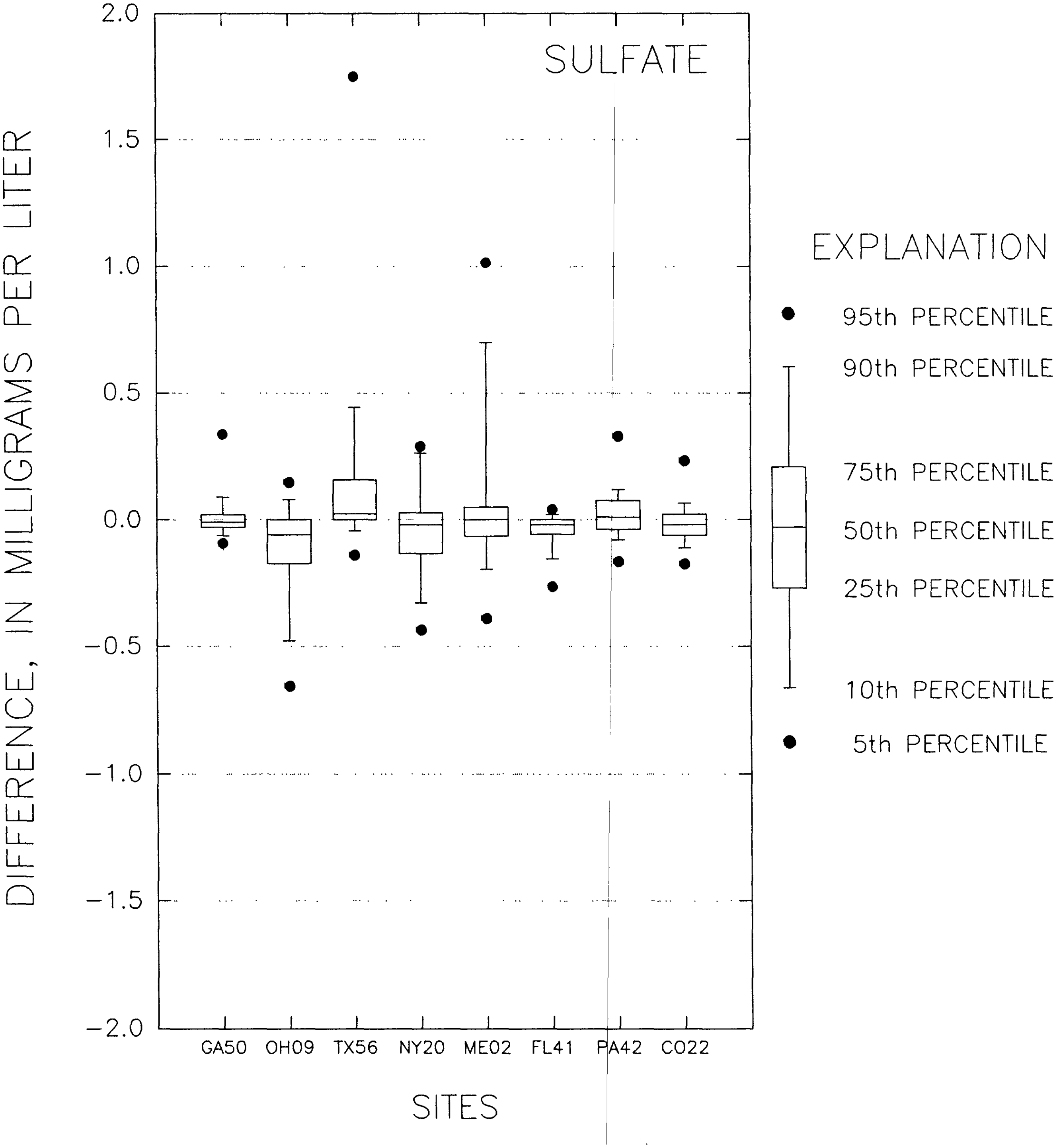

Figure 12.--Difference in sulfate concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

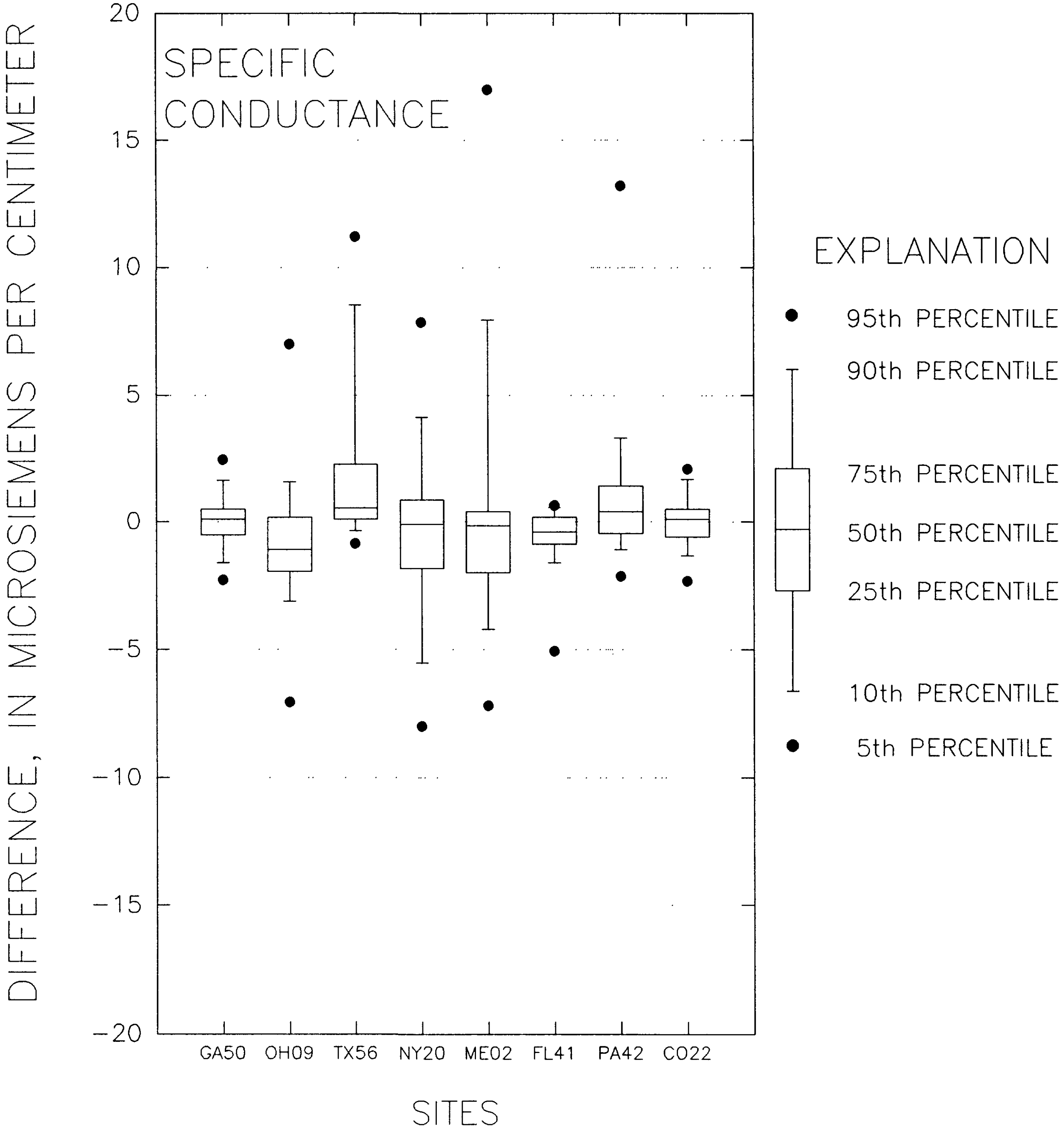

Figure 13.--Difference in hydrogen ion concentration between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

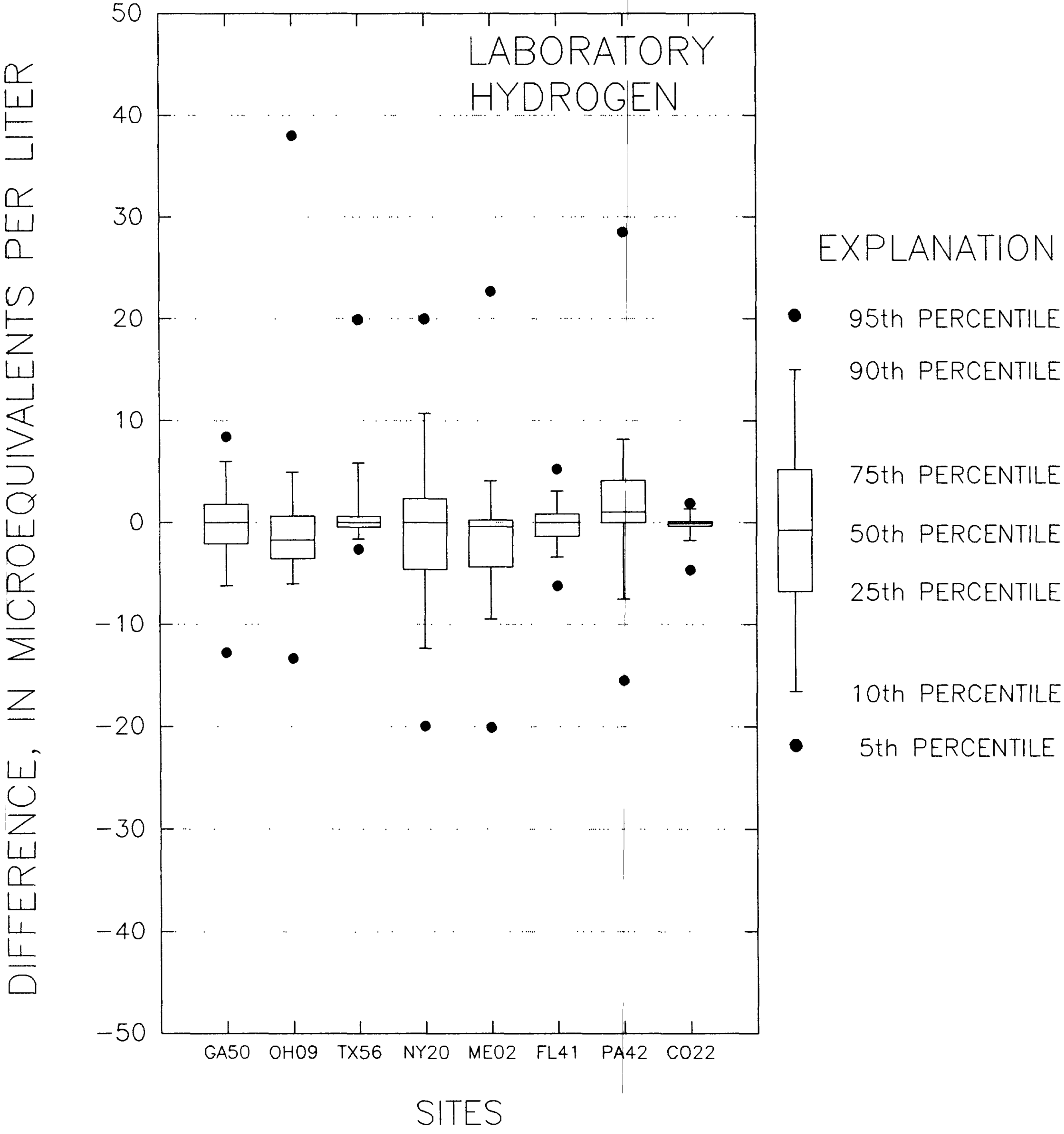

Figure 14.--Difference in specific conductance between samples from original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

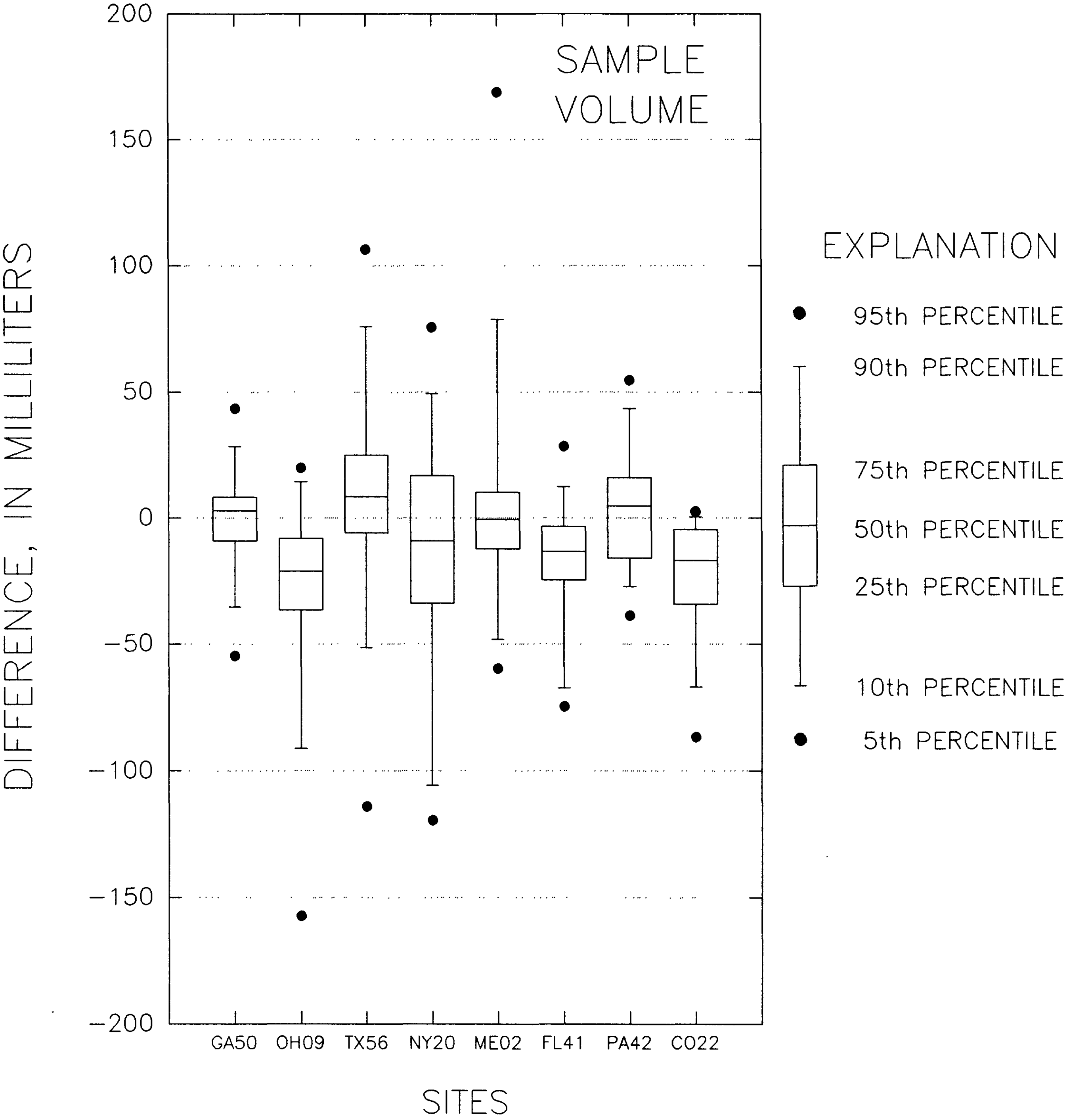

Figure 15.--Difference in collected sample volume between original and collocated samplers at eight sites. [See figure 1 for an explanation of site abbreviations.]

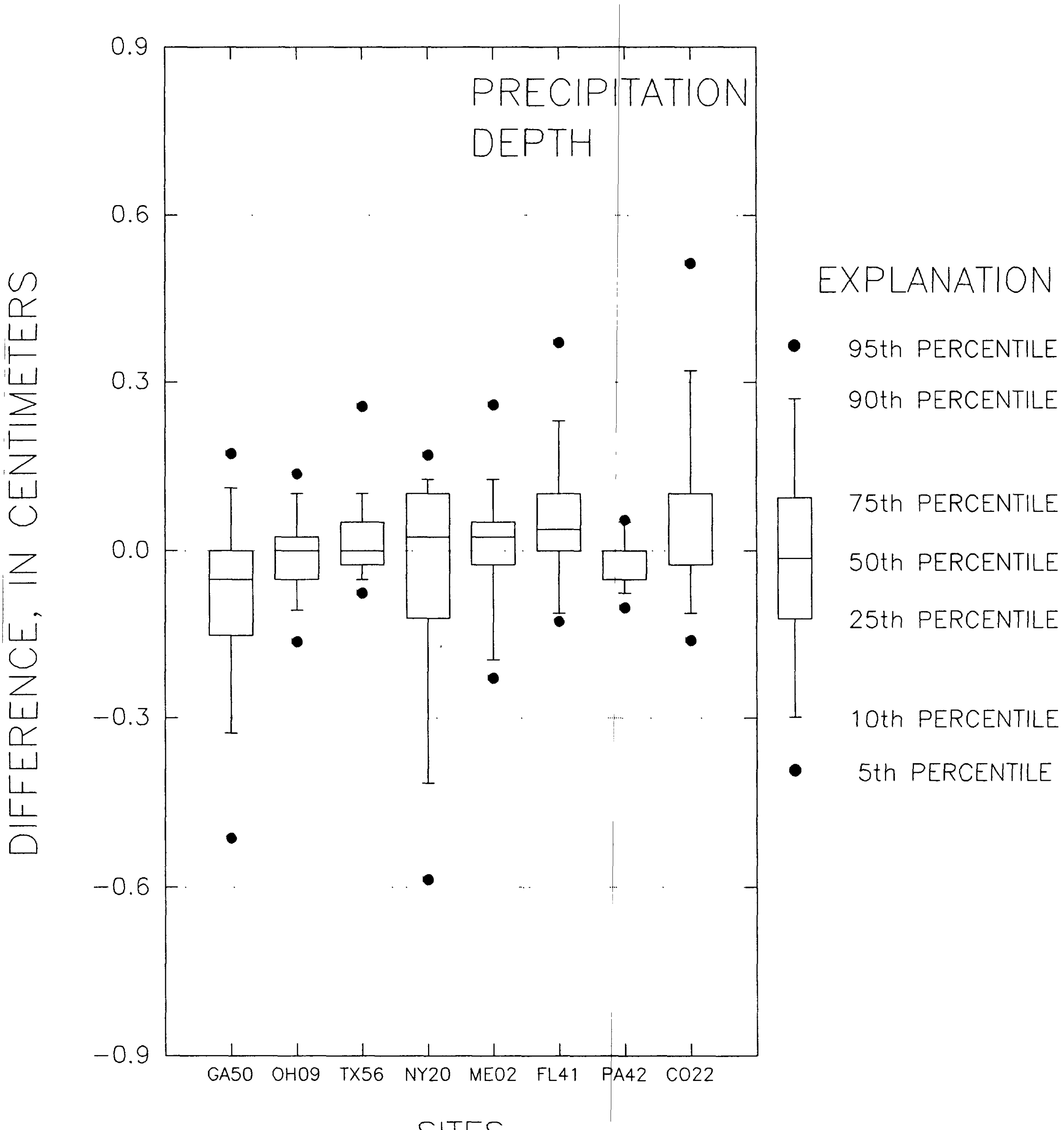

Figure 16.--Difference in precipitation depth between original and collocated rain gages at eight sites. [See figure 1 for an explanation of site abbreviations.]

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