ANALYSIS OF QUALITY-ASSURANCE AND QUALITY-CONTROL PROCEDURES FOR AN URBAN WATER-QUALITY MONITORING PROGRAM, GWINNETT COUNTY, GEORGIA

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Abstract. The U.S. Geological Survey has, during many years of environmental monitoring, developed quality-assurance and quality-control procedures to assist in the collection of accurate and representative water-quality data. Urban storm sampling typically is performed using one of two methods; the equal-width-increment method or the automated-point-sample method. Quality-control data (equipment blanks and concurrent samples) were collected from 1997 to 2006 at 12 watersheds in Gwinnett County, Georgia, to compare these methods and to evaluate the cleanliness of field procedures. Constituent concentrations in samples collected concurrently using both methods were compared to determine how representative point-sample data were of cross-sectional stream conditions. Percent differences of concurrent-sample constituent concentrations were compared with storm size to identify bias or trend when collecting samples using the automated-point-sample method. Data collected using the two different methods indicated that constituent concentrations in concurrent samples generally were within 10 percent. Constituent concentrations in equipment blanks typically were less than analytical method detection limits.

INTRODUCTION

The U.S. Geological Survey (USGS), in cooperation with Gwinnett County Department of Water Resources, established a watershed monitoring program in 1996. The Gwinnett County Watershed Monitoring (GCWM) Program is an urban water-quality monitoring project that includes continuous and discrete water-quality sampling in 12 watersheds located throughout the county (Fig. 1).
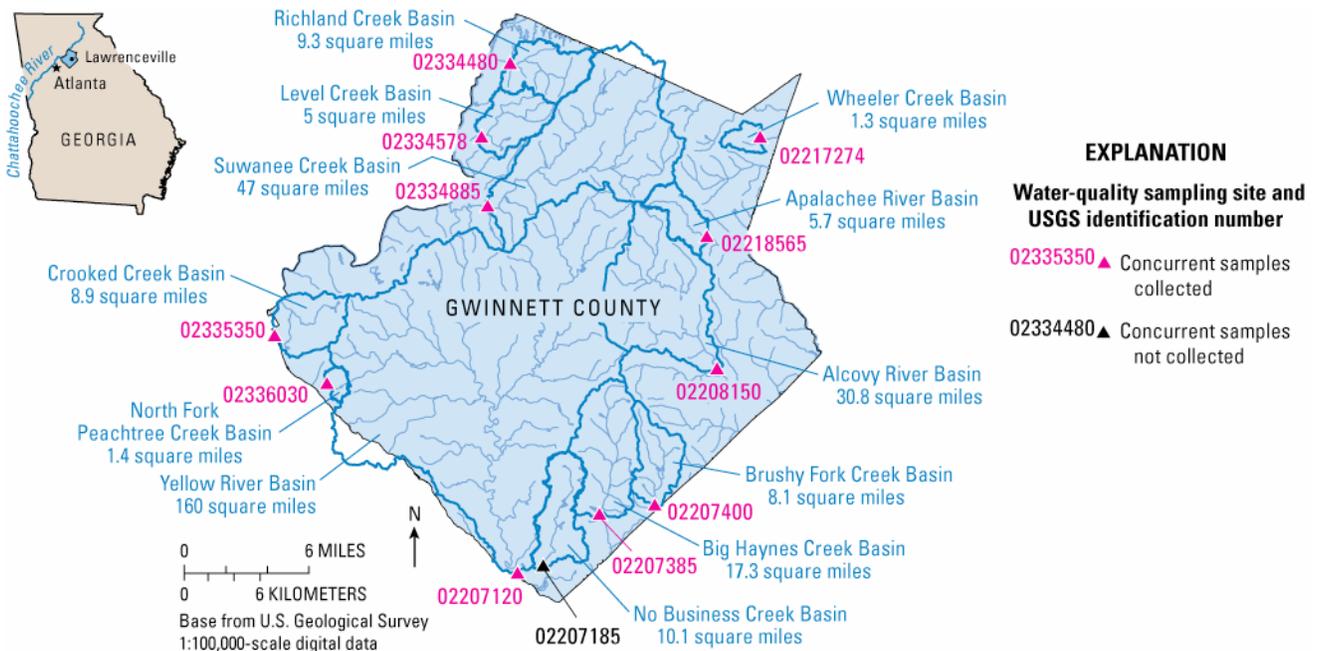

Figure 1. Watershed monitoring program, Gwinnett County, Georgia. Sampling sites where concurrent samples were collected are shown in magenta.

Storms in urban watersheds are characterized by increased runoff, rapid rises in stage, and higher stream velocities than during baseflow. Typically, the GCWM Program uses the equal-width-increment (EWI) sampling method to collect composite water-quality samples to ensure that the samples are representative of conditions throughout the stream cross section. The EWI sampling method divides the stream cross section into equal increments. Samples are collected by lowering and raising a sampler through the water column at the center of each increment (Wilde and others, 1998b, p. 30). To accommodate the rapid response of urban streams to runoff, an automated point sampler (APS) was used for this program instead of the EWI method to collect samples during storms. An APS is a pump with sample tubing installed in a fixed position above the stream bed. For the GCWM Program, the gage height recorder is programmed with a stage-discharge rating curve. The recorder is programmed to begin sampling once a desired gage height threshold has been met. Equal-volume samples are collected after a programmed amount of discharge has passed. An APS collects samples on the rise, peak, and recession of the storm hydrograph. Two types of quality-control (QC) samples were collected for this study: (1) equipment blanks, to assess the quality of field procedures used to clean sample equipment, and (2) simultaneous (concurrent) environmental samples collected by using both EWI and APS methods, to determine how representative APS samples are to cross section composite samples. These are identified in the text that follows as concurrent sample sets.

METHOD

Equipment blanks and concurrent sample sets were collected as part of the QC for the GCWM Program. Blank water, a solution free of analyte(s) of interest at a specified detection level, was used to evaluate the cleaning procedures used for cleaning an APS (Wilde and others, 1998a, p. 61). Blank water was passed through the APS pump tubing and collected in a clean sample collection bottle. The blank water was then processed into bottle sets, preserved with acid, and shipped to a National Environmental Laboratory Accreditation Conference (NELAC) certified laboratory for analysis.

Manual samples were collected using the EWI method at the same time APS samples were collected. Comparisons between the two datasets were analyzed to evaluate how well the constituent concentrations in the APS sample agreed with those in the cross section and whether there was any bias as a function of storm size, or if APS samples are biased when collected during rising, peak, or falling stages of the storm hydrograph.

RESULTS

The equipment blank results and mean storm concentrations are shown in Table 1. Between 55 and 57 equipment blank samples were collected with 12 different APS installed for the GCWM Program from 1997 to 2005. The term *hits* is defined as a sample concentration above the laboratory reporting limit, and excludes estimated sample concentration levels below laboratory reporting limits, but which are above the laboratory detection limits. Five equipment blanks showed detectable concentrations (9 percent) for total suspended solids (TSS). The mean concentration for TSS in those blanks was 5 milligrams per liter (mg/L).

Table 1. Summary of equipment blanks from 1997 to 2005 from 12 automated point samplers.

[mg/L, milligram per liter; <, less than; $NO_2 + NO_3$, total nitrite-plus-nitrate; µg/L, microgram per liter; —, data unavailable]

Constituent	Number of blank samples	Number of blanks below reporting limits	Number of hits[1]	Mean hit concentration	Reporting limits	Mean storm-sample concentration
Total suspended solids	55	50	5	5 mg/L	<1 mg/L	160–1,760 mg/L
Total dissolved solids	55	53	2	6 mg/L	<1 mg/L	38–130 mg/L
Total NO_2+NO_3	55	52	3	0.51 mg/L	<.02 mg/L	0.34–1.1 mg/L
Total phosphorus	56	55	1	0.05 mg/L	<.02 mg/L	0.10–0.66 mg/L
Total copper	57	56	1	5 µg/L	<1 or <2 µg/L	3–37.8 µg/L
Total lead	57	57	0	—	<1 or <2 µg/L	6.6–54.3 µg/L
Total zinc	57	45	12	14 µg/L	<1 or <2 µg/L	27–266.0 µg/L
Dissolved copper	18	0	0	—	<2 µg/L	—
Dissolved lead	18	0	0	—	<2 µg/L	—
Dissolved zinc	18	2	2	2 µg/L	<2 µg/L	—

[1]Number of hits—Hits are samples containing constituent concentrations above laboratory reporting limits.

Two equipment blanks (3.6 percent) had detectable concentrations of total dissolved solids (TDS) above laboratory reporting limits; the mean TDS value was 6 mg/L (Table 1). The mean APS storm-sample concentration collected at all GCWM Program sites for the period 1997–2005 for TDS ranges from 38 to 130 mg/L. One blank contained copper (Cu), another contained phosphorus (P), and three had hits for total nitrite-plus-nitrate (NO_2+NO_3) as nitrogen (N). No equipment blanks had measurable lead (Pb) concentrations. Twelve out of 57 equipment blanks (21 percent) contained zinc. The mean concentration of total zinc, 14 micrograms per liter (µg/L), is below the range of mean storm-sample concentrations (27–266 µg/L). The GCWM Program has modified pre-storm preparations to eliminate contamination during sampling, including more thorough rinses with deionized water, brushing out the end of the sample tubing, and installing a stopper in the sample tubing that will be discharged into the stream during the first APS purge cycle. Sample tubing is also being installed above the water surface during pre-storm flow conditions to avoid algae and sediment buildup in and around the sample tubing.

The APS sample method is used only for the GCWM Program during storm events when streamflows are rising rapidly and manual samples are difficult to collect. Constituent concentrations in concurrent sample sets are shown by site in Table 2. The eleven monitoring sites used in this analysis are located in different watersheds with drainage areas that range from 1.3 to 160 square miles; the 11 sample sites are color coded in Figure 1. In order to compare concurrent samples collected in different watersheds and to determine any bias in results with different storm magnitudes, discharge at the time of concurrent sample collection was normalized to the pre-storm for each site. Storm magnitude was calculated as the ratio of discharge of the concurrent sample to the mean pre-storm discharge for each individual sample. The resulting storm magnitude is dimensionless. An example of why storm magnitude helps to compare concurrent sample set results collected at different watersheds would be site 02207120 on August 30, 2005, and site 02207385 on November 19, 2003 (Table 2). Both sites were sampled at a storm magnitude of 8.9 times greater than their respective pre-storm discharge. Bias or trends would be difficult to analyze and assumptions may be inaccurate if looking strictly at sample discharge. The discharge at the time of sample collection at sites 02207120 and 02207385 was 1,160 cubic feet per second (ft^3/s) and 142 ft^3/s, respectively.

The percent difference between APS constituent concentrations and EWI samples was calculated by dividing the EWI constituent concentrations by the APS constituent concentrations, subtracting 1 and multiplying by 100. Samples with equivalent or zero percent differences in constituent concentrations fall on the equal-value-line in Figure 2. APS samples with greater constituent concentrations than EWI samples are shown in

red in Table 2 and plot to the left of the equal-value line in Figure 2. APS samples with lower constituent concentrations than EWI samples are shown in blue in Table 2 and plot to the right of the equal-value line in Figure 2.

Each set of concurrent samples also are identified as to when they were collected on the storm hydrograph to show any bias in the APS method. All samples, with the exception of four concurrent samples, were collected on the recession of the storm hydrograph. One concurrent sample set was collected at the peak of the hydrograph, and three were collected on the rise. Because more samples need to be collected on the rise of the hydrograph, no bias estimates related to position on the hydrograph could be made.

Twenty-three concurrent sample sets were analyzed for TSS, TDS and total zinc, and 16 of these sample sets were analyzed for dissolved calcium (Ca) and dissolved magnesium (Mg) (Table 2). Nineteen concurrent sample sets were collected on the recession of the storm hydrograph. Of these 19 sets, 89 percent of TSS and 84 percent of total zinc concentrations fell within 10 percent of the equal-value line (Fig. 2). All dissolved Ca and Mg percent differences of the concurrent samples collected on the recession were within 12 percent of the equal-value line (Table 2). The largest outlier for dissolved Ca, 11 percent, had concentrations of 2.5 mg/L collected using the EWI method and 2.8 mg/L collected using the APS method at station 02334885; the same sample yielded 0.63 mg/L vs. 0.70 mg/L, or 10 percent difference for dissolved Mg (Table 2). At station 02335350; the largest outlier for dissolved Mg, 12 percent, had concentrations of 0.66 mg/L and 0.59 mg/L in EWI and APS samples, respectively. Ca concentrations in the same sample set contained 3.4 mg/l (EWI) vs. 3.2 mg/l (APS) or a percent difference of 6 percent (Table 2).

One concurrent sample set collected on the rise of the hydrograph at station 02334885 contained TSS, TDS, and dissolved Mg concentrations that differed by less than 10 percent from the EWI sample. The total zinc and dissolved Ca concentrations for this sample were equal for the EWI and APS samples. This concurrent sample was collected during the second largest storm magnitude of 43.3 times greater than the pre-storm flow (Fig. 2). Another concurrent sample set collected on the rise of the storm hydrograph at station 02334578 had constituent concentrations for TDS, TSS, total zinc, Ca, and Mg that differed less than 7 percent from the EWI sample (Table 2). All three concurrent sample sets collected on the rise of the hydrograph yield higher and lower constituent concentrations for the APS method versus the EWI method and some constituent concentrations are equal (Table 2). One concurrent sample was collected on the peak of a storm hydrograph (Table 2). The TSS and total zinc values differed by 3 and 15 percent, respectively, from the equal-value line (Fig. 2). In addition, the TDS value for this concurrent sample set differed by 23 percent where as dissolved Ca and Mg differed by 1 and 5 percent, respectively.

Table 2. Summary of concurrent samples, samples collected simultaneously using equal-width-increment and automated point sampler sample methods in Gwinnett County, Georgia, from 2001 to 2005.

[USGS, U.S. Geological Survey; ID, identification; sq mi, square mile; ft^3/s, cubic foot per second; *storm magnitude, concurrent sample discharge divided by pre-storm discharge; TDS, total dissolved solids; mg/L, milligram per liter; CEWI/CAPS, constituent concentration of equal-width-increment method divided by automated point sample method; TSS, total suspended solids; µg/L, microgram per liter; —, no data available; EWI, equal-width-increment sample method; APS, automated point sampler method; percent differences calculated (EWI/APS-1)*100; red numbers indicate APS sample method yielded a greater constituent concentration, blue numbers indicate EWI sample method yielded a greater constituent concentration]

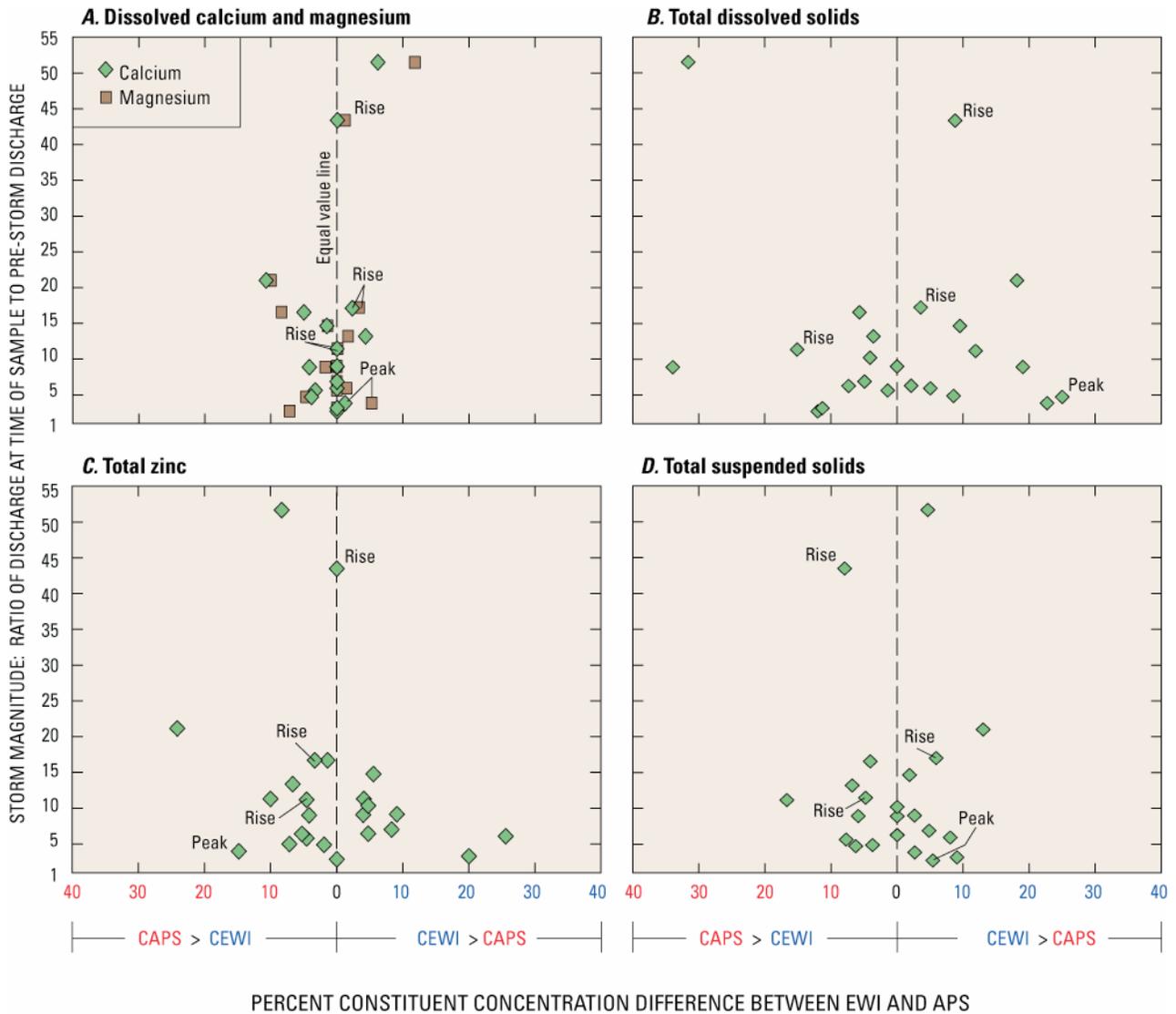| USGS site ID	Sample method	Position on storm hydrograph at time of concurrent sample	Date	Watershed size (sq mi)	Pre-storm discharge (ft^3/s)	Concurrent sample discharge (ft^3/s)	*Storm magnitude	TDS (mg/L)	Percent difference of TDS CEWI/CAPS	TSS (mg/L)	Percent difference of TSS CEWI/CAPS	Total zinc (µg/L)	Percent difference of total zinc CEWI/CAPS	Dissolved calcium (mg/L)	Percent difference, dissolved calcium CEWI/CAPS	Dissolved magnesium (mg/L)	Percent difference, dissolved magnesium CEWI/CAPS
02207120	EWI APS	Recession	7/24/2002	161.5	55	910	16.5	50 53	6	330 344	4	72 73	1	5.7 6.0	5	1.10 1.20	8
	EWI APS	Peak	7/31/2003	161.5	160	614	3.8	81 66	23	115 112	3	23 27	15	8.1 8.0	1	2.00 1.90	5
	EWI APS	Recession	11/20/2003	161.5	110	1,610	14.6	46 42	10	108 106	2	19 18	6	4.5 4.6	2	1.40 1.42	1
	EWI APS	Recession	8/30/2005	161.5	130	1,160	8.9	75 63	19	160 170	6	26 25	4	4.9 4.9	0	1.30 1.30	0
02207385	EWI APS	Recession	7/23/2000	17.3	3.5	22	6.3	47 46	2	130 130	0	22 21	5	— —	—	— —	—
	EWI APS	Recession	11/19/2003	17.3	16	142	8.9	37 56	33	184 184	0	23 24	4	2.3 2.4	4	0.57 0.58	2
02207400	EWI APS	Recession	7/23/2000	8.2	0.7	3.4	4.9	38 35	9	260 270	4	13 14	7	— —	—	— —	—
	EWI APS	Recession	11/19/2003	8.2	5.0	66	13.2	54 56	4	151 162	7	14 15	7	2.4 2.3	4	0.59 0.58	2
02208150	EWI APS	Recession	11/9/2000	30.8	8.5	94	11.1	47 42	12	150 180	17	27 30	10	— —	—	— —	—
	EWI APS	Recession	10/27/2003	30.8	20	54	2.7	44 50	12	39 37	5	7 7	0	5.4 5.4	0	1.30 1.40	7
02217274	EWI APS	Recession	2/24/2005	1.3	1.6	9.5	5.9	79 83	5	87 94	7	17 23	35	2.6 2.6	0	0.67 0.68	1
02218565	EWI APS	Recession	11/9/2000	5.7	8.0	55	6.9	61 58	5	62 65	5	12 13	8	3.8 3.8	0	1.10 1.10	0
02334885	EWI APS	Recession	11/19/2000	47	14	143	10.2	47 49	4	170 170	0	22 21	5	— —	—	— —	—
	EWI APS	Rise	3/28/2000	47	30	1,300	43.3	37 34	9	139 151	8	13 13	0	2.9 2.9	0	0.85 0.84	1
	EWI APS	Recession	8/30/2005	47	70	1,470	21.0	130 110	18	260 230	13	22 29	24	2.5 2.8	11	0.63 0.70	10
	EWI APS	Recession	1/10/2000	47	39	220	5.6	70 71	1	120 130	8	21 22	5	5.9 6.1	3	1.40 1.40	0
02335350	EWI APS	Recession	3/3/2001	8.9	4.0	25	6.3	38 41	7	35 35	0	18 19	5	— —	—	— —	—
	EWI APS	Recession	11/17/2003	8.9	4.0	13	3.2	55 62	11	12 11	9	24 20	20	7.9 7.9	0	1.40 1.40	0
	EWI APS	Recession	11/17/2003	8.9	4.0	36	9.0	46 46	0	39 38	3	36 33	9	5.7 5.7	0	1.40 1.40	0
	EWI APS	Recession	8/5/2004	8.9	3.3	170	51.5	39 57	32	450 430	5	110 120	8	3.4 3.2	6	0.66 0.59	12
02336030	EWI APS	Recession	2/24/2005	1.4	1.4	6.6	4.7	45 36	25	15 16	6	52 53	2	5.0 5.2	4	0.62 0.65	5
02334578	EWI APS	Rise	10/17/2006	5	2.0	33	16.6	46 44	4	170 160	6	31 32	3	4.3 4.2	2	0.90 0.87	3
02334480	EWI APS	Rise	10/17/2006	9.3	6.6	75	11.4	58 68	15	460 480	4	49 51	4	6.2 6.2	0	1.00 1.00	0

Figure 2. Percent constituent concentration difference between equal-width-increment (EWI) method and automated point sample (APS) method for (*A*) dissolved calcium and magnesium, (*B*) total dissolved solids, (*C*) total zinc, and (*D*) total suspended solids. [Rise, concurrent sample collected during the rise of the storm hydrograph; Peak, concurrent sample collected during the peak of the storm hydrograph; CEWI, constituent concentration from equal-width-increment method; CAPS, constituent concentration from automated point sample; >, greater than]

CONCLUSIONS

The U.S. Geological Survey has developed quality-assurance and quality-control procedures for use in the Gwinnett County Watershed Monitoring Program to aid in the collection of accurate water-quality data using the automated point sampler (APS) method. The results of field testing have determined that APS cleaning methods needed to be modified with a more thorough rinse with de-ionized water. Proper installations above stream beds and above pre-storm water surfaces also will help minimize potential sample contamination. The use of APS is critical to collecting samples during the rising, peak, and falling stages of an urban storm hydrograph. Data collected demonstrate that APS samples can be effectively compared to equal-width-increment samples and generally are within 10 percent of each other when sampled on the recession of a storm hydrograph. To collect representative water-quality data, APS need to be strategically located where streams are well-mixed and accessible. APS should be cleaned between every sampled storm, and equipment blanks should be collected and analyzed to ensure that inefficient or improper cleaning of automated point samplers do not compromise water-quality data. More concurrent samples need to be collected in association with greater storm magnitudes and at various points on the storm hydrograph to determine if there is any bias or trend associated with using the APS method.

LITERATURE CITED

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Wilde, F.D., D.B. Radke, J. Gibs, and R.T. Iwatsubo. 1998b. Collection of water samples, National Field Manual for the Collection of Water-Quality Data. Handbooks for Water-Resources Investigations, Techniques of Water-Resources Investigations of the U.S. Geological Survey, pp. 30.