Sediment Dynamics for a Changing Future (Proceedings of the ICCE symposium held at
Warsaw University of Life Sciences - SGGW, Poland, 14–18 June 2010). IAHS Publ. 337, 2010.

The use of instrumentally collected-composite samples to estimate the annual fluxes of suspended sediment and sediment-associated chemical constituents

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Abstract Experience from a long-term water quantity and water quality monitoring network for Atlanta, Georgia, USA, has indicated that many of the problems associated with event based-sampling in small, "flashy" watersheds can be overcome through the use of instrumentally collected (autosamples) flow-weighted composite samples. The benefits of composite samples relative to discrete samples include: (1) the ability to sample a larger number of events during a year; (2) the collection of substantially larger suspended sediment (SS) masses for more accurate and representative chemical and/or physical analyses; and (3) the capability of using composite sample-derived SS and sediment-associated chemical data in conjunction with such variables as maximum event discharge (QMax) and total event water volume (VolTot) to construct rating curves for estimating the SS and sediment-associated chemical fluxes of unsampled events.

Key words autosamplers; storm sampling; suspended sediments; rating curves

INTRODUCTION

Experience in both large and small watersheds has indicated that the majority of suspended sediment and sediment-associated chemical constituents are transported by high-flow and/or storm events (e.g. Horowitz, 1995, 2008, 2009). In large basins like the Mississippi River, more than 85% of the annual fluxes of suspended sediment are transported in conjunction with stormflow. In smaller watersheds, the percentage may be even higher (e.g. Horowitz, 2009). That means that sampling efforts need to be concentrated on storm events to better delimit the annual fluxes of SS and sediment-associated constituents and to establish error limits for unsampled events when estimates are made using a variety of techniques such as rating curves. However, the logisitics of sampling storm events in small watersheds can be extremely difficult as a result of time constraints and traffic congestion (e.g. Horowitz *et al*., 2008; Horowitz, 2009). A potential solution, based on over 5 years of experience in an urban watershed, is described herein.

In 2001, the City of Atlanta, Georgia, (COA) asked the US Geological Survey (USGS) to design and implement a long-term water-quantity and water-quality monitoring program intended to function as a "backbone" for addressing current and future water quality issues/evaluations; however, program implementation did not begin until 2003 (e.g. Horowitz & Hughes, 2006). The sediment-specific program objectives for the COA's monitoring program are encompassed by the following series of questions: (1) Are the COA's sediment-associated chemical concentrations elevated relative to typical background/baseline levels? (2) What are the annual fluxes and specific yields of SS and sediment-associated chemical constituents in the COA's streams? (3) How much of the annual fluxes for selected chemical constituents are transported in association with sediment, and how much are dissolved? (4) How much of the annual fluxes are storm-driven and how much are moved during baseflow? (5) How much of the annual fluxes are derived from point-sources and how much are derived from nonpoint- (diffuse) sources? and (6) Does the COA impact the annual fluxes of SS and sediment-associated constituents within its watersheds and/or in downstream receiving waters? The methods used to address these questions have been amply described elsewhere, and consist of a combination of manual sampling during both baseflow and stormflow in conjunction with the extensive use of autosamplers to collect the majority of the stormflow samples (e.g. Horowitz & Hughes, 2006; Horowitz *et al*., 2008; Horowitz, 2009).

Ten long-term sites were equipped with autosamplers configured to operate with 24, 1-L bottles, and programmed to start collecting samples after a minimum rise (typically ~4.5 cm, depending on the site) within a 15-minute interval. Subsequent aliquots were collected at fixed temporal intervals (also depending on the site) that coincided with discharge measurements (every 15 minutes) to facilitate flux calculations. Each "sample" consisted of a triad of polyethylene bottles; hence, each autosampler could collect up to 8 temporally spaced-aliquots. The aliquots were timed to distribute the samples over the rising limb, the peak, and the falling limb of the storm hydrograph. The contents of the 2 outer bottles were used to determine SS concentration (SSC) and sediment chemistry whereas the middle bottle was used to determine a variety of dissolved constituents (USGS, various). As a result of the autosampler configuration, as well as resource limitations, only 5 or 6 storms could be sampled per site per year (e.g. Horowitz, 2009).

Site-specific rating curves (e.g. Fig. 1(a)) were used to estimate annual SS fluxes for each location (e.g. Horowitz, 2009; Horowitz, unpublished data). In 2004 and 2005, COA streams discharged about 150 000 tonnes of SS to downstream receiving waters. The annual loads dropped substantially in the following three years due to a long-term drought (100 000, 33 000 and 26 000 tonnes). Regardless, the majority of the annual SS loads (typically >94%) were transported in conjunction with stormflow that also accounted for ≥65% of the annual discharge. Depending on the site, specific yields ranged from just over 30 to more than 1000 t km^{-2}; however, typical mean/median specific yields during normal rainfall exceeded 300 t km^{-2} (Horowitz, 2009; Horowitz, unpublished results). Not surprisingly, the mean/median specific yields declined during the drought. During normal rain years, between 30 and 50 storms occur; however, the total time for these events usually amounts to ≤20% (≤50 days) of the year. Based on comparisons with actual (manual or auto) samples, the estimation errors associated with the rating-curve derived annual SS flux estimates ranged from –23 to +27%, but the absolute mean errors were markedly lower, averaging 11% for the 10 sites over 5 years. This absolute mean error is well within the limits usually associated with measuring discharge and SSC (e.g. Horowitz, 2003, 2008, 2009, unpublished data).

Another major objective of the COA monitoring program is to determine the annual fluxes of various sediment-associated chemical constituents to evaluate the impact of the COA on downstream water quality, as well as to identify any temporal water-quality trends. It would have been useful, as well as cost-efficient, to apply the same rating curve technique for estimating SSC, to dissolved and suspended sediment-associated chemical fluxes using either discharge and/or turbidity as a surrogate as has been done elsewhere (e.g. Christensen, 2001; Goolsby *et al*., 2001; Vanni *et al*., 2001; Rasmussen *et al*., 2005; Stelzer & Likens, 2006; Rasmussen, *et al*., 2008). Initial data evaluations indicated that unlike previous studies, the most useful surrogate for the COA program appeared to be SSC (e.g. Horowitz, 2009). Under "ideal" circumstances (e.g. for Cu and Zn), when actual SSC values were available, sediment-associated chemical concentration estimation errors were on the order of ±30 to 35% (e.g. Horowitz, 2009). Unfortunately, when actual SSC values were unavailable, and rating curve-derived SSCs had to be used *in lieu* of actual measurements to estimate sediment-associated chemistry, the mean absolute errors increased to about 90%. Hence, this approach appeared inapplicable in the COA's watersheds.

When this situation occurred before, sediment chemical fluxes were estimated using annual mean/median concentrations derived from actual baseflow and stormflow samples (e.g. Horowitz, 1995, 2008; Horowitz, *et al*., 2001). In these prior cases, the majority of the sediment-associated constituent concentrations displayed limited interannual variability (usually within and/or close to the analytical errors associated with generating the data), despite substantial differences in annual discharge and/or SSC (e.g. Horowitz, 1995; Horowitz *et al*., 2001). The interannual variability of the median chemical concentrations for the COA sites are substantially greater than the analytical errors associated with them, but generally less than a factor of two (Horowitz *et al*., 2008).

Based on annual median dissolved and sediment-associated chemical concentrations for baseflow and stormflow, with the exception of total N (TN), ≥75% of the annual fluxes of trace elements (e.g. Cu, Pb, Zn), major elements (e.g. Fe, Mn, Al), and total P (TP) occur in association with suspended sediment; in turn, ≥90% of the transport occurs in conjunction with stormflow. Sediment-associated TN fluxes range from 50 to 60% of the annual total; even so, storm-related TN fluxes typically exceed 80% of the annual load. Lastly, based on the dominance of stormflow relative to the annual fluxes of suspended sediment, trace/major elements, and nutrients, it would appear that most of this material is derived from nonpoint (diffuse)-sources.

Unfortunately, the errors associated with estimating the annual fluxes of sediment-associated chemical constituents using annual median concentrations for baseflow and stormflow were markedly greater than those associated with the annual estimates for suspended sediment fluxes, and in some cases, exceeded 200% (Horowitz, 2009, unpublished data). This probably resulted from two factors: (1) the relatively limited number of actual storm events (5 or 6 out of 30–50 per year) that could be collected using the autosampler configuration described previously, and (2) the lack of a usable surrogate for estimating sediment-associated concentrations in the absence of actual samples. The apparent remedy for this situation entails collecting more storm samples for subsequent chemical analyses. To that end, the autosampler configuration and sampling protocols were changed (e.g. Horowitz, *et al*., 2008; Horowitz, 2009). The revision calls for collecting more (20–30) composite storm samples that should permit better estimates of stormflow chemistry and hence, better annual flux estimates (e.g. Horowitz, 2009).

The autosampler configuration was changed from 24 1-L (l) bottles to a single 20-L bottle. The sampling program itself is based on the collection of fixed volume (~200 ml), flow-weighted, whole-water storm composites. The 200-ml volume was selected to permit collection of 80-subsample composites without overfilling the single sample bottle (16 L in a 20-L capacity container, plus a margin of safety). Flow-weighting is site-specific, and means that more of the 80 subsamples are collected during the high-flow portion of each storm. Based on 2004/2005 data, appropriate flow-weights were determined to permit the complete sampling of up to a 90th percentile storm. After collection, the storm composites are analysed for both dissolved and sediment-associated constituents. Unsampled storm chemistry would be estimated by selecting applicable data from the analysed composites based on: (1) discharge, (2) precipitation, and (3) length of antecedent dry conditions, or by using the actual composite samples to generate sediment-associated chemical rating curves.

RESULTS AND DISCUSSION

The revised sampling effort using the newly configured autosamplers and sampling protocol began around mid-2007; initial data evaluations began 18 months later at the end of 2008. Depending on the site, between 25 and 48 composite storm samples were collected during that period, and represented between 51 and 73% of the total site-specific events. Sampled events ranged in time from a few hours to several days, composite SSCs ranged from 20 mg L^{-1} to almost 1900 mg L^{-1}, whereas calculated fluxes from individual composites ranged from 2 to 7600 t. Minimum, maximum, mean and median concentrations for a selection of sediment-associated chemical constituents indicate that COA event related-suspended sediments continue to display elevated concentrations of Cu, Pb, Zn, Cd, Ni, Hg, Fe and total organic carbon (TOC); suspended sediment-associated TN is well above US EPA ecoregion 45 criteria (US EPA, 2000). These results mirror those collected previously (e.g. Horowitz *et al*., 2008; Horowitz, 2009).

A number of benefits resulted from the switch from individual to composite autosamples. The new approach provides many more event-related samples per year (from 3 (15 years^{-1}) to 5 (25 years^{-1}) times more) for each monitoring site. This much larger number of samples, in conjunction with the much larger sample masses available from the composite (20 L), as opposed to individual sample bottles (1 L), generated more representative and precise measurements of storm-related sediment chemistry. Further, the enhanced sediment chemical data also provided much better estimates of annual mean/median sediment-associated chemical concentrations.

However, two of the findings from the revised sampling program were rather unexpected, and resulted from an initial analysis of the composite sample data in conjunction with some of the continuous measurements (e.g. discharge, turbidity) obtained at each site. These results provided an alternative approach for estimating both the annual fluxes of suspended sediment, as well as those for sediment-associated chemical constituents for unsampled events. In the first instance, it became apparent that the event-specific SS fluxes calculated from the composite samples could be used in conjunction with measured/calculated values for event-specific maximum discharge (Q_{Max}) and/or total water volume (Vol_{Tot}) to generate rating curves for estimating event-specific SS fluxes for unsampled events (Tables 1 and 2, Fig. 1(b)). The rating curves are site-specific and were generated in the normal way; however, instead of using individual SSCs or SS fluxes in conjunction with individual measures of discharge or turbidity, calculated measures of total event-related flux from the composite samples were substituted for the former, and values for either Q_{Max} or Vol_{Tot} were substituted for the latter. The estimates for annual site-specific SS fluxes using both traditional and composite approaches tend to fall within the range of errors typically associated with measuring discharge and SSC, as well as those with estimating annual SS fluxes using traditional rating curve methods (on the order of ±15 to 20%; e.g. see Horowitz, 2003; 2008). As such, both sets of flux estimates appear comparable (Tables 1 and 2).

It should be noted that in the particular case of the COA streams sampled in this study, Q_{Max} simply represents the maximum discharge measured during the course of an individual event. This accrues because the differences between baseflow and stormflow discharge tend to be on the order of one to three orders of magnitude; hence, baseflow contributions are inconsequential. At other locations, where baseflow may make a significant contribution to stormflow, hydrographic separation may be required to obtain a more accurate estimate for Q_{Max} (e.g. Wahl & Wahl, 1995).

The calculated SS fluxes from actual composite samples can be used in conjunction with both normal and composite rating curves to generate accurate estimates of annual SS fluxes in one of three ways. First, the composite samples can be used to validate existing rating curves based on discharge and/or turbidity (e.g. Fig. 1(a)) as well as for providing error estimates for the annual SS fluxes. Second, the calculated fluxes from the composite samples can be combined with estimates from the discharge and/or turbidity rating curves (e.g. Fig. 1(a)) to estimate annual SS fluxes for both unsampled events, and for baseflow. Lastly, the calculated fluxes from the composite samples can be combined with estimates from the composite rating curves based on either Q_{Max} or Vol_{Tot} (Fig. 1(b)) to derive annual SS flux estimates (Tables 1 and 2).

As noted previously, attempts to estimate sediment-associated chemical concentrations for unsampled events using traditional rating curve/surrogate approaches employing measured sediment chemical data from the individual (1-L) sample bottles with selected surrogates (e.g. turbidity, SSC), failed to provide usable results (e.g. Horowitz, *et al.*, 2008; Horowitz, 2009). However, unlike the results from site-specific rating curves derived from the individual sample bottles, those derived from site-specific composite samples (Fig. 1(c),(d)) do appear to generate acceptable estimates of sediment-associated chemical (at least for Cu and Zn) fluxes (Tables 1 and 2). Note that the two most appropriate surrogates for estimating sediment chemical fluxes are either total SS fluxes or Q_{Max} for each event (composite sample). The interrelationship between chemistry and total SS fluxes seems stronger than for Q_{Max}; therefore it would appear to be the surrogate of choice for estimating sediment chemistry (Fig. 1(c),(d)). However, the advantage gained by using total SS fluxes *in lieu* of using Q_{Max} only holds in the case of actual composite samples where the total SS fluxes can be calculated rather than estimated. In the case of unsampled events, when total SS fluxes first have to be estimated with a rating curve (e.g. Fig. 1(b)), and that value used in conjunction with a composite sediment chemical flux curve (e.g. Fig. 1(c),(d)) there is little difference from the results obtained using Q_{Max} (Tables 1 and 2). Please note that this approach appears to work well for estimating total sediment-associated chemical fluxes for periods of a year or more; however, estimates for single events can differ significantly from the actual calculated values (Tables 1 and 2).

Table 1 Various measurements and rating-curve derived estimations for flow-weighted composite samples collected at the Peachtree Creek 2 site, Atlanta, Georgia, USA.

									Est. From Meas. SS Flux		Est. From Est. SS Flux		Est. From $Q_{(Max)}$			Est. From Meas. SS Flux		Est. From Est. SS Flux		Est. From $Q_{(Max)}$	
Date	Time	Mea. SSC (mg/L)	Calc. Comp. SS Flux (tonnes)	Est. Pred. SS Flux (Q) (tonnes)	Est. Cor. Pre. SS Flux (T) (tonnes)	Est. Cor. Pre. SS Flux (Q_{max}) (tonnes)	Est. Cor. Pre. SS Flux (Vol_{Tot}) (tonnes)	Calc. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Calc. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)
2/13/07	15:01	50	18	41	33	59	110	1.3	1.0	1.0	3.5	3.9	4.0	4.7	5.3	5.7	6.3	16	19	19	23
2/25/07	05:46	58	24	46	29	59	130	1.6	2.0	2.0	3.9	4.4	4.0	4.7	5.8	8.2	9.1	18	22	19	23
3/1/07	07:45	878	2700	2200	1400	1200	1200	140	160	160	140	160	80	93	690	720	800	630	750	500	600
4/3/07	22:01	142	82	60	110	80	190	5.3	8.0	8.2	5.3	6.0	6.0	7.0	26	35	39	25	30	27	32
5/11/07	18:31	392	92	47	76	240	70	14	9.0	9.2	4.0	4.5	19	22	52	40	44	19	22	89	110
6/11/07	18:00	596	130	25	81	86	61	19	12	12	1.9	2.1	7.0	8.2	81	58	64	8.7	10	29	34
6/19/07	20:46	387	160	120	130	350	130	17	15	15	11	13	28	33	77	72	79	53	63	130	160
6/28/07	20:46	484	390	320	400	350	280	39	35	36	29	33	28	33	180	170	190	140	160	130	160
7/8/07	05:01	286	210	220	190	320	250	17	20	20	21	23	25	29	71	94	100	98	120	120	140
7/10/07	16:10	262	220	150	240	130	290	19	21	22	14	16	10	12	83	98	110	67	80	46	55
7/14/07	10:46	189	160	100	180	97	280	11	15	15	9.3	10	8.0	9.3	51	72	79	44	52	33	39
7/19/07	17:01	171	160	69	170	78	320	15	15	15	6.2	6.9	6.0	7.0	51	72	79	29	34	26	31
7/25/07	20:01	514	330	230	280	280	220	27	30	31	21	24	22	26	100	140	160	100	120	100	120
8/24/07	20:16	447	510	300	470	260	390	47	44	45	28	31	21	24	240	210	230	130	160	95	110
8/29/07	15:31	368	160	84	190	120	140	12	15	15	8	8.6	9.0	10	58	72	79	36	43	39	46
8/30/07	16:31	398	220	220	210	390	180	21	21	22	21	23	30	35	77	98	110	98	120	150	180
9/13/07	14:31	343	160	96	150	160	150	13	15	15	8.9	9.9	13	15	61	72	79	42	50	58	69
9/14/07	08:34	445	590	590	490	430	470	55	50	51	50	56	33	38	210	240	270	240	290	160	190
10/4/07	08:34	180	48	26	67	64	80	2.9	4.0	4.1	2.0	2.3	5.0	5.8	23	19	21	9.1	11	21	25
2/1/08	00:41	356	21	2.2	2	17	15	1.7	2.0	2.0	0.1	0.1	1.0	1.2	7.7	6.9	7.7	0.3	0.3	5.0	6
2/17/08	17:07	733	660	550	550	510	310	51	55	56	47	53	39	45	230	260	290	220	270	200	240
2/21/08	14:13	266	240	560	320	800	320	18	22	23	48	54	57	66	750	110	120	230	270	320	380
2/26/08	06:45	522	550	530	540	390	350	49	47	48	46	51	30	35	220	230	260	220	260	150	180
3/4/08	08:45	202	200	350	240	270	350	16	19	19	32	35	21	24	76	89	99	150	180	98	120
3/7/08	05:51	124	140	240	130	190	390	11	13	13	22	25	15	17	51	62	69	110	130	68	81
3/19/08	13:17	372	430	510	390	390	390	37	38	39	44	49	30	35	160	180	200	210	250	150	180
3/29/08	18:35	149	140	240	140	190	340	14	13	13	22	25	15	17	54	62	69	110	130	69	82
4/4/08	21:09	142	230	630	270	350	610	21	22	23	53	59	28	33	100	100	110	250	300	130	160
4/11/08	20:44	324	380	350	340	260	420	38	34	35	32	35	21	24	150	160	180	150	180	95	110
4/26/08	19:23	241	390	560	380	630	590	43	35	36	48	54	47	55	180	170	190	230	270	250	300
5/11/08	04:36	255	170	200	180	190	230	17	16	16	19	21	15	17	81	76	84	89	110	69	82
5/15/08	14:19	163	130	250	130	200	280	13	12	12	23	26	16	19	63	58	64	110	130	73	87
5/23/08	15:15	342	270	200	370	160	280	30	25	26	19	21	13	15	240	120	130	89	110	57	68
6/11/08	16:10	411	250	140	210	320	200	27	23	24	13	15	25	29	110	110	120	62	74	120	140

6/28/08	16:04	268	47	23	56	64	51	4.7	4.0	4.1	1.7	1.9	5.0	5.8	21	19	21	7.6	9.0	21	25
7/6/08	12:26	380	120	64	100	210	92	15	11	11	5.7	6.4	16	19	58	53	59	27	32	74	88
7/8/08	23:59	462	190	140	180	250	130	6.7	18	18	13	15	20	23	38	85	94	62	74	91	110
7/10/08	14:36	206	36	13	46	49	51	2.7	3.0	3.1	0.8	0.9	3.0	3.5	16	14	15	3.7	4.4	16	19
7/13/08	10:47	648	420	410	300	720	220	42	37	38	37	41	52	61	170	180	200	170	210	280	330
7/29/08	19:33	410	120	79	120	200	92	11	11	11	7.3	8.1	16	19	46	53	59	34	40	70	83
7/31/08	12:47	326	140	130	150	320	140	17	13	13	12	14	25	29	68	62	69	58	69	120	140
8/2/08	18:54	221	79	50	120	80	110	8.7	7.0	7.2	4.3	4.8	6.0	7.0	32	34	38	20	24	27	32
8/13/08	22:45	151	41	27	50	83	81	3.8	3.0	3.1	2.1	2.3	6.0	7.0	17	16	18	9.3	11	28	33
8/17/08	19:44	189	140	170	150	180	250	15	13	13	16	18	15	17	73	62	69	76	90	66	78
8/25/08	13:53	236	360	680	370	590	550	34	33	34	57	63	44	51	130	160	180	270	320	230	270
10/8/08	11:06	340	480	750	640	630	510	44	42	43	61	68	47	55	200	200	220	290	340	250	300
10/17/08	11:43	83	43	71	54	86	170	4	4.0	4.1	6.4	7.2	7.0	8.2	20	17	19	30	36	29	34
12/24/08	23:33	831	1200	390	380	340	510	98	89	91	35	39	27	31	490	420	470	170	200	130	160
Totals			14000	13000	12000	13000	13000	1200	1200	1200	1100	1200	1000	1200	6000	5500	6100	5200	6200	5100	6000
Mean Absolute Error			N/A	110	74	140	140	N/A	3.1	3.0	8.7	9.2	9.9	11	N/A	29	35	51	59	54	56
Max. Overestimate				400	160	560	380		16	20	32	38	39	48		47	110	150	190	110	170
Max. Underestimate				–810	–1300	–1500	–1500		–9	–7	–63	–59	–71	–66		–650	–630	–530	–480	–430	–370

Table 2 Various measurements and rating-curve derived estimations for flow-weighted composite samples collected at the South River 1 site, Atlanta, Georgia, USA.

									Est. From Meas. SS Flux		Est. From Est. SS Flux		Est. From $Q_{(Max)}$			Est. From Meas. SS Flux		Est. From Est. SS Flux		Est. From $Q_{(Max)}$	
Date	Time	Mea. SSC (mg l^{-1})	Calc. Comp. SS Flux (t)	Est. Pred. SS Flux (Q) (t)	Est. Cor. Pre. SS Flux (T) (t)	Est. Cor. Pre. SS Flux (Q_{max}) (t)	Est. Cor. Pre. SS Flux (Vol_{Tot}) (t)	Calc. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Pred. Cu Flux (kg)	Cor. Pred. Cu Flux (kg)	Calc. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)	Pred. Zn Flux (kg)	Cor. Pred. Zn Flux (kg)
6/28/07	21:48	966	89	32	44	79	18	15	14	15	12	13	12	13	70	73	77	65	69	61	70
7/8/07	06:42	271	21	17	19	26	14	2.7	2.8	2.9	3.5	3.7	3.2	3.7	15	17	18	20	22	19	22
7/11/07	14:23	31	1	2	3	5	8	0.2	0.1	0.1	0.6	0.6	0.5	0.6	1.5	1.0	1.1	4.1	4.4	3.8	4.4
7/20/07	16:28	77	5	2	4	6	14	0.5	0.7	0.7	0.7	0.8	0.6	0.7	3.7	4.6	4.9	5.0	5.3	4.5	5.2
7/29/07	16:02	294	69	60	82	74	53	9.7	11	11	12	12	11	13	49	56	60	60	64	57	65
8/23/07	21:29	228	9	3	8	8	8	0.9	1.2	1.3	0.9	0.9	0.8	0.9	5.8	7.8	8.3	5.8	6.2	5.5	6.3
8/28/07	12:49	90	3	2	4	5	6	0.4	0.4	0.4	0.6	0.6	0.5	0.6	2.1	3.1	3.3	4.1	4.4	3.8	4.4
8/29/07	16:23	230	18	9	17	18	15	3.5	2.3	2.5	2.4	2.5	2.1	2.4	18	14	15	14	15	13	15
8/30/07	16:50	139	5	1	4	5	6	0.3	0.5	0.6	0.6	0.6	0.5	0.6	1.9	3.9	4.1	4.1	4.4	3.8	4.4
9/11/07	08:47	223	13	5	12	12	12	2.1	1.6	1.7	1.4	1.5	1.3	1.5	13	10	11	9.2	9.8	8.6	10
9/13/07	15:28	225	27	17	23	19	25	4.9	3.7	3.9	2.5	2.7	2.4	2.8	25	22	23	15	16	15	17
9/14/07	15:56	222	75	76	83	92	80	11	11.7	12	15	16	14	16	61	61	65	75	80	71	81

10/4/07	10:09	238	15	10	17	19	12	2.9	1.9	2.0	2.5	2.7	2.3	2.6	16	12	13	15	16	14	16
10/22/07	09:55	98	22	26	39	20	49	5.2	2.9	3.1	2.7	2.8	2.5	2.9	31	18	19	16	17	15	17
11/15/07	03:12	77	3	2	3	4	8	0.3	0.3	0.3	0.5	0.5	0.4	0.5	4.4	2.3	2.4	3	3.5	2.9	3.3
12/15/07	17:19	87	15	25	21	20	39	3.7	1.9	2.0	2.7	2.8	2.5	2.9	23	12	13	16	17	15	17
12/28/07	08:41	372	110	91	110	120	68	23	18	19	20	21	18	20	100	90	96	98	110	87	100
1/10/08	00:59	118	2	1	1	1	3	0.4	0.2	0.2	0.1	0.1	0.1	0.1	2.3	1.5	1.6	0.8	0.9	1.0	1.2
1/31/08	20:45	127	47	100	70	48	88	7.1	6.9	7.3	7.1	7.6	6.5	7.5	36	38	40	39	41	36	41
2/17/08	18:41	196	41	38	51	44	46	7.9	5.9	6.3	6.4	6.8	6.0	6.9	38	33	35	35	38	33	38
2/21/08	14:45	70	35	150	79	56	120	5.9	4.9	5.3	8.4	8.9	7.9	9.1	33	28	30	45	48	43	49
2/26/08	08:09	234	58	56	54	42	55	8.7	8.7	9.3	6.0	6.4	5.6	6.4	47	47	50	34	36	32	36
3/4/08	10:02	93	21	46	28	31	52	3.4	2.8	2.9	4.3	4.6	4.0	4.6	20	17	18	25	26	23	27
3/7/08	06:20	101	35	61	32	43	80	3.0	4.9	5.3	6.2	6.6	5.7	6.5	22	28	30	34	37	32	37
3/19/08	13:27	366	190	150	160	160	130	32	33	35	28	29	26	29	140	150	160	130	140	120	140
4/27/08	00:57	104	25	24	20	10	53	3.0	3.4	3.6	1.1	1.2	1.1	1.3	35	20	21	7.5	8	7.2	8.3
5/11/08	03:25	598	270	150	190	190	110	43	50	53	33	36	34	38	210	230	240	160	170	160	180
5/15/08	15:13	150	35	53	33	30	52	3.2	4.9	5.3	4.1	4.4	3.8	4.4	20	28	30	24	26	22	26
7/5/08	13:51	408	180	130	160	140	110	31	32	34	24	25	22	26	150	150	160	120	120	110	130
7/8/08	15:02	190	59	82	81	58	72	7.1	8.9	9.5	8.7	9.3	8.2	9.4	34	48	51	47	50	44	50
7/29/08	18:17	410	26	5	11	16	12	3.7	3.5	3.8	2.0	2.2	1.8	2.1	17	21	22	13	13	11	13
8/2/08	20:11	138	17	14	15	16	25	1.1	2.2	2.3	2.0	2.2	1.8	2.1	6.6	13	14	13	13	12	13
8/7/08	15:45	239	9	3	8	9	6	1.0	1.1	1.1	1.0	1.1	1.0	1.1	4.6	7.0	7.4	6.7	7.1	6.5	7.5
8/12/08	22:31	72	5	3	4	4	12	0.2	0.5	0.6	0.5	0.5	0.4	0.5	1.9	3.9	4.1	3.3	3.5	2.9	3.3
10/8/08	07:25	370	98	78	86	120	61	19	16	17	20	21	19	21	110	80	86	98	110	92	110
10/17/08	13:01	74	12	20	11	15	36	1.2	1.5	1.6	1.9	2.0	1.8	2.1	9.1	9.8	10	12	13	11	13
10/24/08	08:51	62	11	22	10	14	40	1.1	1.4	1.5	1.7	1.9	1.6	1.8	8.9	8.9	9.5	11	12	10	12
12/10/08	10:38	273	73	93	100	93	61	14	11	12	15	16	14	16	72	59	63	76	81	72	82
12/11/08	11:17	43	12	57	15	44	67	1.0	1.5	1.6	6.4	6.8	5.9	6.8	6.0	9.8	10	35	38	33	38
12/24/08	23:59	137	36	62	44	54	59	6.0	5.0	5.4	8.0	8.5	7.5	8.6	39	29	30	43	46	41	47
Totals			1800	1800	1800	1800	1800	290	280	300	280	290	260	300	1500	1500	1600	1400	1500	1400	1600
Mean Absolute Error			N/A	20	11	10	25	N/A	1.1	1.3	1.8	1.8	1.8	1.7	N/A	6.0	6.9	8.5	8.4	8.9	8.2
Max. Overestimate				120	45	32	85		7.0	10	5.4	5.8	4.9	5.8		18	32	29	32	27	32
Max. Underestimate				–120	–80	–80	–160		–4.9	–2.7	–9.5	–7.3	–9.5	–5.4		–29	–24	–51	–41	–53	–30

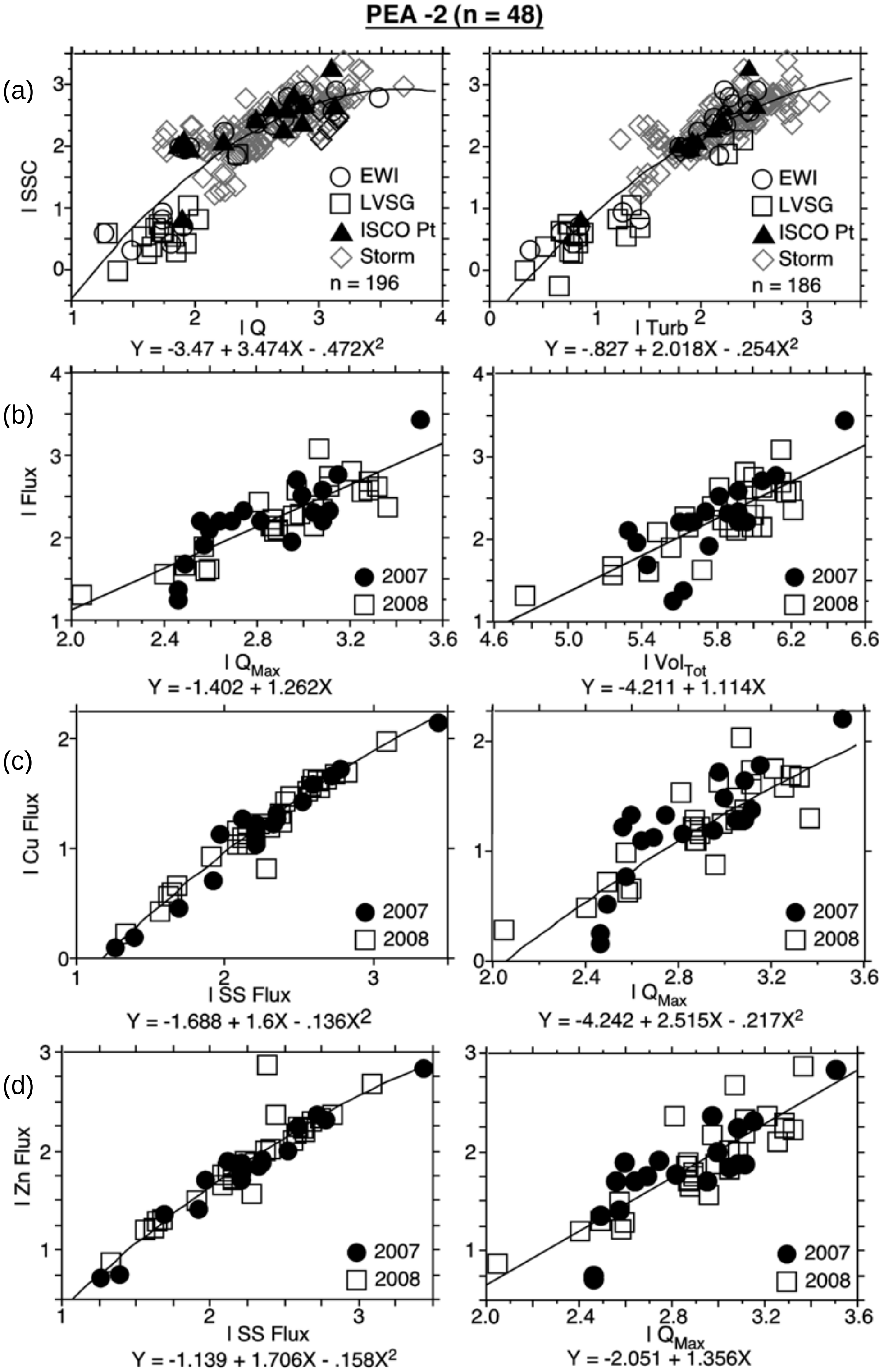

Fig. 1 A group of rating curves for the Peachtree Creek 2 site. Group (a) are standard rating curves for estimating suspended sediment concentration (SSC) from either discharge (Q) or turbidity (Turb) and were generated from four types of sample data: EWI (manually collected depth-and-width integrated samples; LVSG (large volume surface grabs collected during baseflow); ISCO PT (samples pumped through the autosampler during collection of the EWI sample; and Storm (individual autosample bottles collected during a storm event). Group (b) contains composite rating curves for estimating suspended sediment fluxes using either maximum event discharge (Q_{Max}) or total event volume (Vol_{Tot}). Groups (c) and (d) are composite rating curves used for estimating the sediment-associated fluxes of Cu and Zn using either total event suspended sediment flux (SS Flux) or maximum event discharge (Q_{Max}).

SUMMARY

(1) Experience from a long-term urban water quantity and water quality monitoring network has indicated that many of the problems associated with event based-sampling in small, “flashy” watersheds can be overcome through the use of instrumentally collected (autosamples) flow-weighted composite samples.

(2) The benefits of composite samples relative to discrete samples include the ability to sample a larger number of events during a year, and the collection of substantially larger SS masses for more accurate and representative chemical and/or physical analyses.

(3) Composite sample-derived suspended sediment and sediment-associated chemical data can be used in conjunction with such variables as maximum event discharge (Q_{Max}) and total event water volume (Vol_{Tot}) to construct rating curves for estimating the SS fluxes of unsampled events.

(4) SS flux estimates derived from composite rating curves appear to be on a par with estimates derived from normal rating curves based on individual samples using such conventional surrogates as discharge or turbidity.

(5) Composite sample-derived sediment-associated chemical data may be used in conjunction with such variables as total SS flux or maximum event discharge (Q_{Max}) to construct rating curves for estimating the fluxes of sediment-associated-chemical constituents, at least for Cu and Zn, for unsampled events.

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