Measuring the fluxes of suspended sediment, trace elements and nutrients for the City of Atlanta, USA: insights on the global water quality impacts of increasing urbanization

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Abstract During 2004 and 2005, suspended sediment fluxes from the City of Atlanta amounted to about 150 000 t year^{-1}; ≥94% of the transport occurred in conjunction with stormflow, which also accounted for ≥65% of the annual discharge; typically, stormflow occurred during ≤20% of the year. Based on annual median chemical concentrations for baseflow and stormflow, the annual fluxes of ≥75% of trace elements (e.g. Cu, Pb, Zn), major elements (e.g. Fe, Al) and total P were sediment-associated; in turn, ≥90% of this transport was storm-related. As such, baseflow sediment-associated and all dissolved contributions represent a relatively insignificant portion of the total annual load. An exception is total N, whose sediment-associated fluxes range from 50 to 60%; even so, storm-related transport exceeded 80% of the total.

Key words Atlanta City; global water quality; suspended sediment; trace elements; urbanization

INTRODUCTION

From the mid-20th century to the start of the 21st century, world urban growth has increased. Projections to 2050 indicate that, while the growth rate may be declining, it will remain substantial, with the percentage of the world's population living in cities rising from 29% in 1950 to 67% in 2050 (UN Development Programme, 2005; World Urbanization Prospects, 2006). Hence, the need, size, complexity and number of urban water-quality studies also are likely to increase. Urbanization affects local landscapes, and the quantity and quality of nearby rivers and streams. Typical effects are detailed elsewhere (e.g. Driver & Troutman, 1989; Ellis, 1999; Horowitz *et al*., 1999; Rose & Peters, 2001; Goodwin *et al*., 2003; Old *et al*., 2003; Leeks *et al*., 2006).

In 2001, the US Geological Survey (USGS), in conjunction with the City of Atlanta (COA), implemented a water-quantity and water-quality monitoring programme to function as a "backbone" for addressing water quality issues/evaluations. The objectives for the programme are: (1) consolidate all water-quality monitoring into a single consistent programme; (2) determine current water-quality conditions; (3) locate sources of water-quality impairment; (4) document water-quality changes in response to infrastructural improvements; (5) assess long-term water-quality trends; and (6) over time, as data accrue, adjust the network to address changing issues, limit costs and improve effectiveness (Horowitz *et al*., 2005; Horowitz & Hughes, 2006). Initial site surveys and site selection, as well as equipment procurement and installation occurred during 2002 and well into 2003 (Fig. 1). Actual sample collection and analyses began in late 2003.

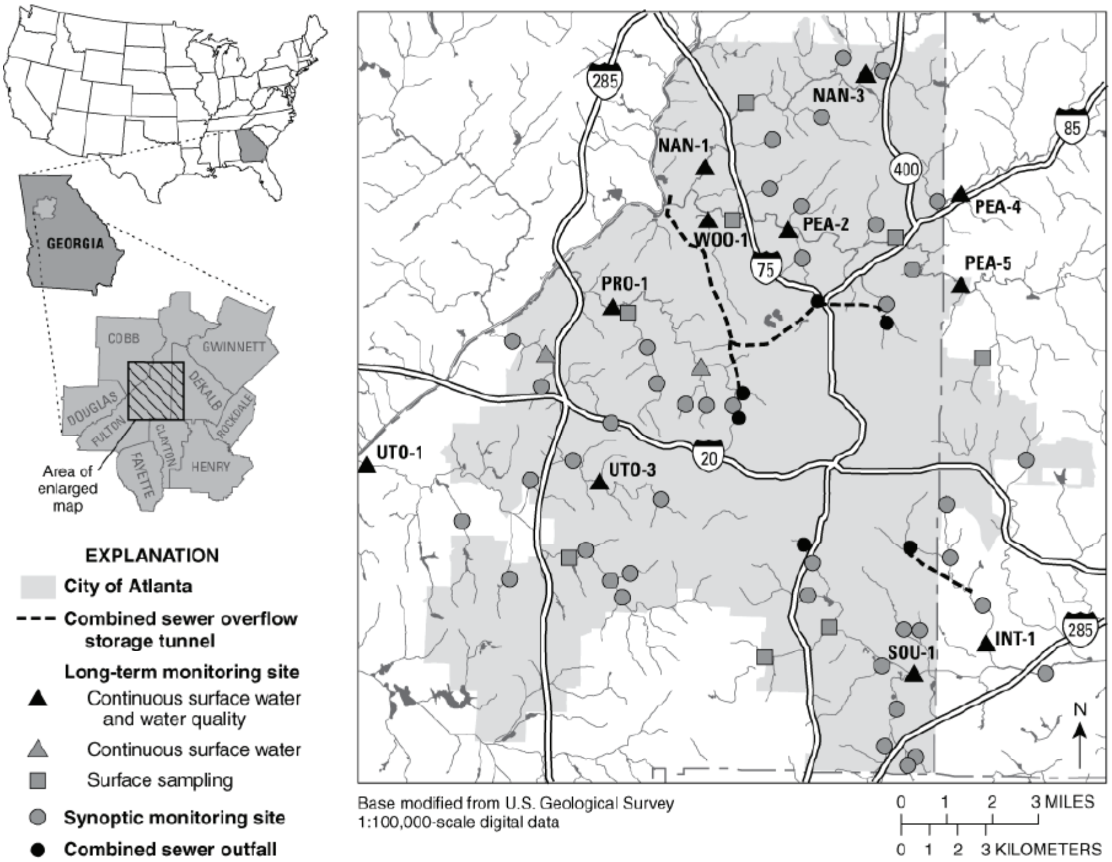

Fig. 1 Location map for the City of Atlanta water-quality and water-quantity monitoring programme; the fully-instrumented sites are marked with a solid triangle: NAN: Nancy Creek; PEA: Peachtree Creek; WOO: Woodall Creek; PRO: Proctor Creek; UTO: Utoy Creek; SOU: South River; and INT: Intrenchment Creek.

Many of the problems, approaches and results associated with operating urban hydrology monitoring networks have been detailed in the literature (Driver & Troutman, 1989; Ellis, 1999; Larsen *et al*., 1999; Rose & Peters, 2001; Goodwin *et al*., 2003; Old *et al*., 2003; Leeks *et al*., 2006). A description of the approaches, problems and initial results encountered during programme start-up and implementation for the COA network may offer some additional help in focusing limited resources in similar, large-scale urban hydrology programmes. As such, the initial results (2004–2005) from the COA monitoring programme, covering the annual fluxes of suspended sediment, trace elements, major elements and nutrients, are described herein.

PROGRAMME DESIGN AND METHODS

The COA water-quality monitoring network consists of 21 long-term sites (Fig. 1). Eleven are “fully instrumented” for real-time measurements of water temperature, pH, specific conductance, dissolved oxygen, turbidity (a surrogate for suspended sediment concentration, SSC), water level (gauge height, a surrogate for discharge) and rainfall; these parameters are measured every 15 min. Two sites only measure water level and rainfall. The remaining eight sites are used to assess water quality. All the fully-instrumented sites are equipped with programmable refrigerated autosamplers to capture stormflow because substantial suspended sediment, sediment-associated, and dissolved chemical transport occur at these times (e.g. Horowitz, 1995; Peters & Kandell, 1999; Rose & Peters, 2001). Only data from the fully-instrumented sites are discussed herein.

The real-time data are complemented with manual sampling consisting of the collection of scheduled and non-convective storm samples. Manual sampling follows standard USGS depth- and width-integrated isokinetic procedures to ensure the collection of cross-sectionally representative samples (e.g. Edwards & Glysson, 1999). Each site is sampled 12 times per year; however, due to the linkage between discharge and water quality, scheduling is not calendar- but hydrologically-based, with the intention of collecting samples covering at least 80–85% of the annual discharge range (e.g. Horowitz, 1995).

The manual sampling programme provides data on chemical parameters that cannot be obtained with real-time measuring equipment (e.g. trace elements, nutrients). It also is used to calibrate/validate the real-time data sondes, and the material collected by the autosamplers. This accrues because the sondes and samplers are at fixed positions in each stream cross-section; thus, the equipment collects point measurements/samples that may not be cross-sectionally representative (e.g. Horowitz, 1995; Edwards & Glysson, 1999). To evaluate this issue, and to develop appropriate correction factors, if necessary, a series of concurrent (two simultaneous) measurements/samples have to be collected over a range of flow conditions. Both samples are then analysed for the same constituents (e.g. SSC, trace elements, nutrients) and compared. Analytical procedures are detailed elsewhere (Horowitz *et al.*, 2005; Horowitz & Hughes, 2006). When necessary, appropriate correction factors are developed so that the data derived from the autosamples and sondes are cross-sectionally representative (e.g. Horowitz, 1995).

RESULTS AND DISCUSSION

Flux calculations

The metric of choice for determining spatial and temporal trends in the COA monitoring programme is annual flux. Initially, the fluxes of suspended sediment and dissolved and sediment-associated constituents were to be calculated by summing a series of daily instantaneous fluxes for each calendar year using the following formula:

$$Flux\ (\text{t d}^{-1}) = Q \times Conc. \times 0.00245$$

where Q is mean daily discharge (ft^3 s^{-1}) and *Conc.* is concentration (mg L^{-1}).

Fluxes are converted to metric units by using an appropriate constant (Porterfield, 1977). Suspended sediment-associated constituent fluxes were to be determined using the same formula. However, as the chemical analyses were performed on dewatered and dried material, concentrations had to be converted from mass mass^{-1} (e.g. mg kg^{-1}) to mass volume^{-1} (e.g. mg L^{-1}) units. Initial annual flux estimates for SSC, using the above-cited approach, in conjunction with site-specific sediment rating curves, were lower than expected. Subsequent analyses of flow duration curves and SSC data raised questions about the applicability of using mean daily discharge (a single daily time-step calculation), to estimate annual fluxes for the relatively "flashy" COA urban streams. Subsequent detailed calculations for sites in the network indicated that the use of mean daily discharge, in conjunction with a single SSC value obtained from a site-specific sediment rating curve, could produce underestimates of annual sediment loads from 25 to nearly 65% (Table 1). Hence, all estimates were calculated using 15-min time steps, although longer periods could have produced annual flux estimates within the range of errors (±15–20%; Table 1) associated with the measurement of discharge and SSC (e.g. Horowitz, 2003).

A drawback to using shorter than daily time steps is missing data; a substantial issue in urban hydrology (e.g. vandalism, damaged equipment, trash in the water). When there are insufficient data to actually determine a mean-daily discharge, the USGS infers a value based on available data and/or in conjunction with measured values from nearby sites; this approach cannot be employed to fill the 15-min record. Hence, the mean-daily discharge record is almost invariably more complete than the record of 15-min values. Even so, when annual fluxes are calculated using mean daily discharges (even enhanced with inferred values), and compared with estimates based on 15-min time step calculations, the latter still generates higher flux estimates; albeit, the differences are less than those cited in Table 1. Therefore, all the fluxes cited herein were calculated using 15-min time steps.

A drawback to using fluxes for determining trends accrues because, by their nature, they reflect changes in flow. Hence, low-flow years typically have lower annual fluxes than high-flow years, regardless of potential environmental changes. To limit this problem, flow-weighted concentrations (annual flux/annual discharge) will be used to evaluate interannual trends when there are marked differences in interannual discharge.

Table 1 Examples of the effects of using different calculation time steps in estimating annual suspended sediment fluxes.

	Intrenchment Creek at Constitution Parkway (INT-1)		Nancy Creek at Rickenbacker Way (NAN-3)		Utoy Creek at Great Southwest Parkway (UTO-1)	
Sampling frequency (hours)	Annual flux (t)	Affect on flux estimate (%)	Annual flux (t)	Affect on flux estimate (%)	Annual flux (t)	Affect on flux estimate (%)
24	9 600	–64	13 000	–49	28 000	–38
12	15 000	–43	18 000	–27	35 000	–23
8	20 000	–28	21 000	–17	39 000	–15
6	20 000	–25	22 000	–12	41 000	–10
4	23 000	–16	23 000	–6	42 000	–8
3	24 000	–13	24 000	–4	43 000	–6
2	25 000	–8	24 000	–2	43 000	–5
1	26 000	–3	25 000	–1	44 000	–3
0.25	27 000		25 000		46 000	

Concurrent sampling

During the first two full years of the programme approx. 100 concurrent samples were collected under a range of flows at the fully-instrumented sites and subsequently analysed. The results indicate that for a majority of the concurrent samples, there is little difference between concentrations (suspended sediment and sediment-associated constituents) obtained from material collected with the autosamplers and that collected manually (e.g. NAN-1, SOU-1; Fig. 2). A number of concurrent samples displayed markedly different SSCs, but similar chemistries (e.g. NAN-3; Fig. 2) or similar SSCs, but dissimilar chemistries (e.g. PEA-5; Fig. 2). In a few cases, neither the SSCs nor the chemistries matched. However, no consistent bias was detected. Taken as a whole, and viewed in conjunction with a knowledge of the range of short-term spatial and temporal SSC and chemical variability often displayed by suspended sediment collected at the same site (e.g. Horowitz, 1995), it appears that during stormflow, cross-sectional suspended sediment distributions are relatively homogeneous. Further, during baseflow, SSC is so low (≤5 mg L^{-1}) that cross-sectional inhomogeneities are unlikely. Hence, correction factors would not substantially improve the data quality from either the sondes or the autosamplers.

Site-specific rating curves and annual estimates of suspended sediment flux

At the end of 2005, using data from samples collected manually or with the auto-samplers, it was possible to construct a series of site-specific sediment rating curves to predict SSC (Fig. 3). Each set consists of two curves and regression equations: (1) SSC *vs* discharge (Q), and (2) SSC *vs* turbidity (FTU: formazine turbidity units). Either curve can be used to predict SSC in the absence of actual samples. Note that while the general shapes of the rating curves (and their concomitant regression equations) for sites within the same watershed tend to be similar, they are not interchangeable (Fig. 3). Typically, the SSC *vs* turbidity rating curve had a higher R^2 than the concomitant SSC *vs* discharge curve, because the SSC and turbidity relationship is more direct than with discharge (e.g. Walling & Webb, 1981, 1988; Christensen, 2001). Unfortunately, at least for the 2004–2005 period, the turbidity records had substantially more missing data than the discharge records at most of the sites (Table 2). Hence, the majority of the predicted SSC values used to estimate annual suspended sediment and sediment-associated chemical constituent fluxes were generated from the SSC *vs* discharge rating curves.

The data for 2004–2005 reveal important patterns of suspended sediment transport in general, and in urban environments in particular (Table 2). With the exception of the Utoy Creek 3 (UTO-3) site in 2004, ≥94% of the sediment transport, and with few exceptions, ≥66% of the annual water discharge occurred in conjunction with stormflow. Stormflow typically was limited ≤20% of the year. While the relative contributions from the different sites varied between 2004 and 2005, partially as a result of differing amounts of missing data, the overall sediment fluxes from the COA watersheds were about 150 000 t $year^{-1}$ (Table 2) and specific yields could exceed 500 t km^2 $year^{-1}$. Annual water discharge from the COA did not substantially change from 2004 (0.33×10^6 m^3) to 2005 (0.36×10^6 m^3); also, 2004 (+15%) and 2005 (+7%) were slightly above average (~1250 mm $year^{-1}$) rainfall years (National Climate Data Center, 2006).

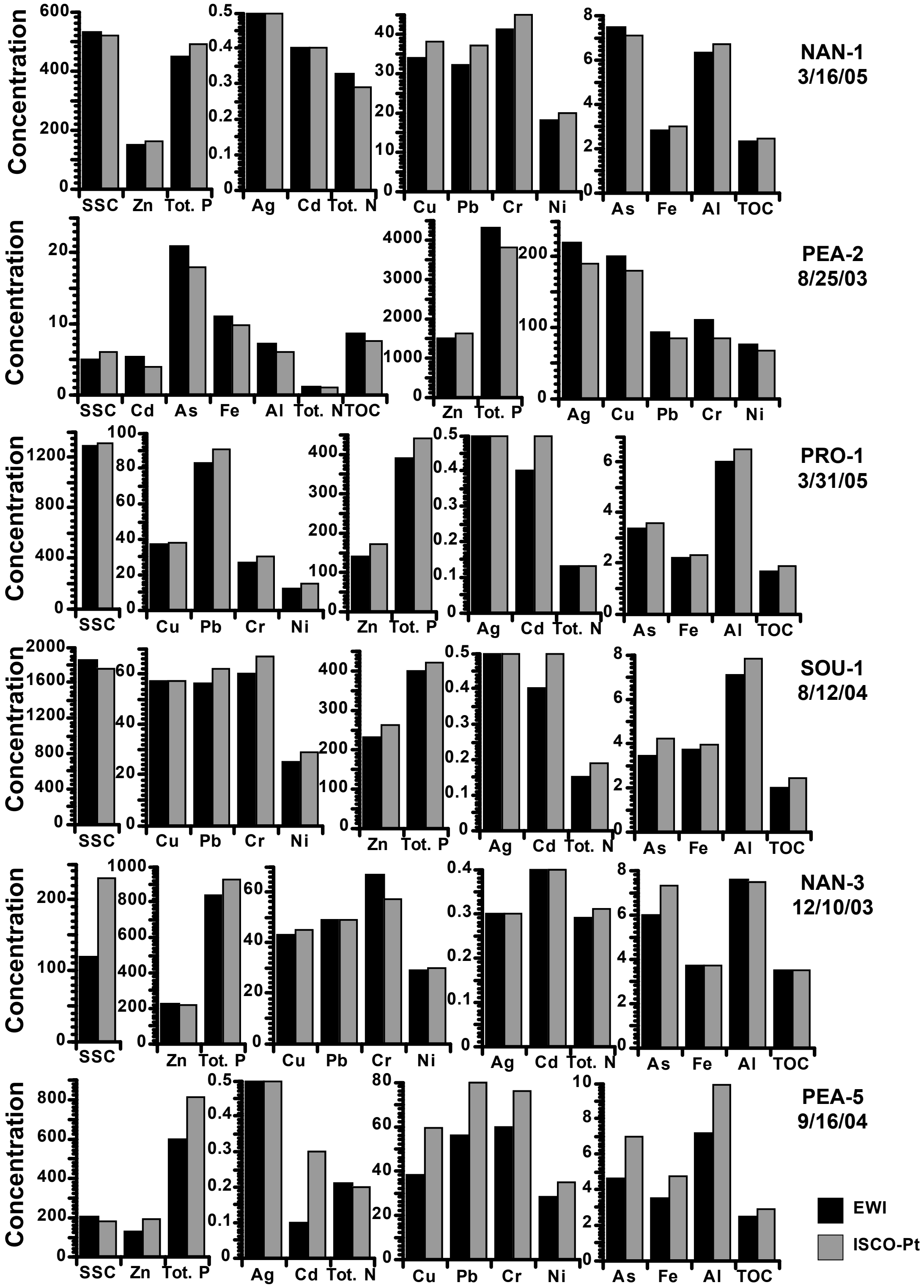

Fig. 2 Selected concurrent sample (simultaneous manual (EWI) and autosampler (ISCO PT)) results for SSC and suspended sediment-associated constituent concentrations from various fully-instrumented sites. The NAN-3 data are from a concurrent sample that had markedly different SSC but similar chemistries, whereas the PEA-5 sample had similar SSCs but markedly different chemistries. The units for the various constituents are: SSC (mg L^{-1}), Ag, Cu, Pb, Cd, Cr, Ni and As (mg kg^{-1}) and total P, total N, TOC, Fe and Al (wt. %).

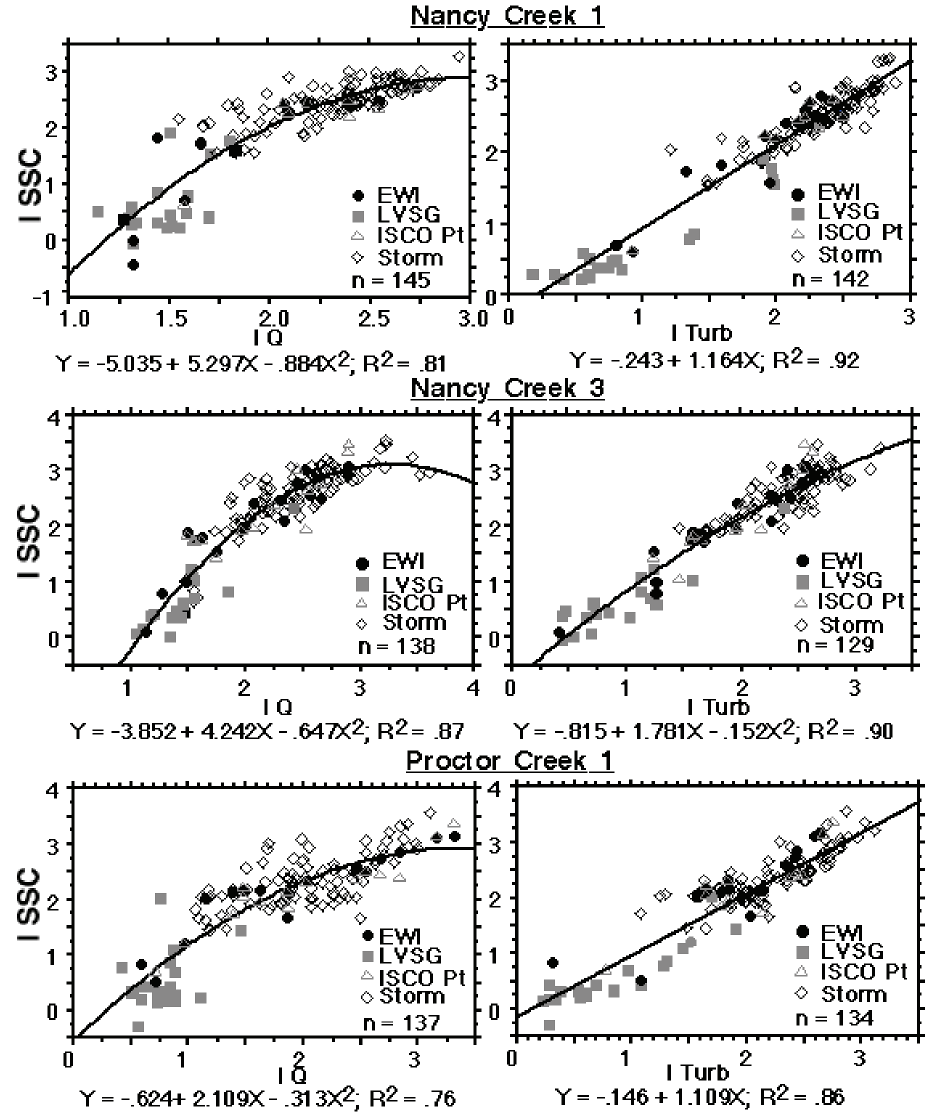

Fig. 3 Sediment rating curves for three sites. Note that although the two Nancy Creek sites are <10 river km apart, the curves/regression equations are not interchangeable. The axes labels represent: log of suspended sediment concentration (l SSC), log of discharge (l Q), and log of turbidity (l Turb). The sample types are: manual isokinetic equal width increment (EWI), manual large volume surface grab (LVSG), simultaneous (with the EWI) autosampler pumped sample (ISCO PT), and a storm sample collected with the autosampler (Storm).

Annual fluxes of suspended sediment, trace elements, major elements and nutrients

The majority of suspended sediment-associated and dissolved chemical concentrations display marked spatial, temporal and hydrological (baseflow *vs* stormflow) variability (Table 3(a) and (b)). The median stormflow concentrations for most sediment-associated constituents are substantially lower than those collected during baseflow, probably as a result of the incorporation of coarser-grained material that contains lower

Table 2 Summary of the estimated annual suspended sediment fluxes for the COA sites for 2004 and 2005 and associated errors. (Total = NAN-1 + PEA-2 +SOU-1 + INT-1 +PRO-1 + UTO-1 = 150 000 tonnes).

Sample Site	Predicted annual flux (tonnes)	% of event-related flux	Ann. vol. × 10^6 (m^3)	% of event-related water	% of year for events (%)	No. calib'n samples	Actual calib'n flux (tonnes)	Predict calib'n flux (tonnes)	Est. error (%)	Missing data (days)	Ind. variable
	2004										
NAN - 3	25 000	>99	51	69	19	62	830	750	–10	6.8	Q*
NAN - 1	18 000	99	59	67	19	77	230	220	–5	4.4	Q
PEA - 4	27 000	>99	62	77	19	83	548	485	–11	3.0	Q
PEA - 5	18 000	>99	51	72	18	49	359	320	–11	1.6	Q
PEA - 2	36 000	>99	136	75	35	64	337	308	–9	15	Q + T[1]
SOU-1	14 000	98	37	66	14	79	270	228	–16	2.7	Q
INT-1	27 000	94	20	62	6	72	797	718	–10	8.9	Q
PRO-1	8 600	94	17	67	9	58	202	200	–1	28.7	Q
UTO-3	3 200	86	11	58	7	42	39	45	15	7.9	T + Q
UTO-1	46 000	>99	59	76	18	54	80	87	9	23.1	T + Q
									Total	*102.1*	
	2005										
NAN - 3	20 000	98	51	66	18	39	158	197	25	32.9	T + Q
NAN - 1	16 000	98	54	60	16	46	201	182	–10	31.0	Q
PEA - 4	22 000	99	65	75	19	50	214	249	17	7.4	Q
PEA - 5	21 000	99	60	73	18	46	87	99	13	10.6	Q
PEA - 2	48 000	99	161	79	29	62	414	422	2	19.8	Q
SOU-1	8 900	97	34	64	15	56	104	123	23	10	Q
INT-1	12 000	97	17	64	8	49	141	179	27	4.8	Q
PRO-1	9 600	99	23	73	11	46	169	145	–14	41.5	Q
UTO-3	3 200	97	8	66	8	63	23	28	22	36.5	T + Q
UTO-1	56 000	99	71	74	18	58	160	148	–8	1.1	Q
									Total	*194.5*	

Q* – discharge; T[1] – turbidity.

Table 3 Summary of median concentrations for suspended sediment-asociated and dissolved constituents for 2004/2005 from the fully instrumented COA sites.

Table 3(a) Sediment-associated constituent concentrations. All concentrations in units of mg kg^{-1}. Continues opposite.

Site Name	Flow	Type	Cu	Pb	Zn	Cd	Cr	Ni	Ba	Fe	Mn	Al	TP	TN
Intrenchment Creek @ Constitution Pkwy	Base	Md.	92	103	355	1.5	90	48	480	7 200	1 200	7 800	3 600	10 000
	Storm	Md.	81	100	290	0.8	70	40	440	47 000	880	86 000	1 200	4 000
South River @ Forest Park Road	Base	Md.	150	94	860	2.9	130	87	420	84 000	2 300	77 000	2 400	9 000
	Storm	Md.	98	110	530	1.5	75	45	400	42 000	2 100	74 000	930	3 500
South Fork Peachtree Creek @ Johnson Rd.	Base	Md.	69	73	370	0.6	140	75	510	70 000	1 900	74 000	2 200	8 900
	Storm	Md.	59	62	265	0.5	67	30	490	37 000	1 200	73 000	870	3 300
North Fork Peachtree Crk @ Buford Hwy	Base	Md.	53	49	360	0.6	75	37	460	67 000	2 400	79 000	1 600	8 100
	Storm	Md.	38	41	240	0.4	38	16	510	34 000	1 800	80 000	700	3 300
Peachtree Crk @ Northside Drive	Base	Md.	99	84	390	0.9	95	62	500	66 000	1 900	78 000	2 600	9 000
	Storm	Md.	62	62	270	0.5	46	21	520	36 000	1 100	80 000	880	3 900
Nancy Creek @ Rickenbacker Dr.	Base	Md.	57	48	270	0.5	79	48	440	60 000	1 900	57 000	1 800	7 800
	Storm	Md.	38	40	210	0.3	46	24	500	34 000	1 200	70 000	670	2 000

Continues opposite

Site Name	Flow	Type	Cu	Pb	Zn	Cd	Cr	Ni	Ba	Fe	Mn	Al	TP	TN
Nancy Creek @ West Wesley Road	Base	Md.	53	58	260	0.4	120	62	520	56 000	2 300	67 000	1 800	7 400
	Storm	Md.	51	52	240	0.4	56	29	510	36 000	1 700	73 000	885	3 800
Proctor Creek @ State Road 280	Base	Md.	64	95	260	0.9	72	35	405	42 000	860	36 000	2 350	9 800
	Storm	Md.	76	110	280	0.7	46	25	450	38 000	880	79 000	1 000	4 200
North Fork Utoy Creek @ Peyton Rd	Base	Md.	55	87	300	0.5	79	37	540	59 000	2 100	74 000	2 100	8 100
	Storm	Md.	38	70	200	0.5	39	19	540	30 000	1 200	59 000	1 000	2 100
Utoy Creek @ Great South-west Pky	Base	Md.	85	86	1 400	0.8	115	69	605	76 000	1 750	100 000	2 300	6 500
	Storm	Md.	70	68	665	0.6	65	39	620	45 000	1 550	100 000	1 000	4 100
Background*			30	25	120	1.0	30	30	600	30 000	600	55 000	1 000	500

* from Horowitz *et al.* (1991).

Table 3(b) Dissolved constituent concentrations. All in concentrations are $\mu g\ L^{-1}$ except TP and TN which are $mg\ L^{-1}$.

	Flow	Type	Cu	Pb	Zn	Cd	Cr	Ni	Ba	Fe	Mn	Al	TP	TN
Intrenchment Creek @ Con-stitution Pkwy	Base	Md.	2.4	0.3	13	0.07	0.2	1.6	50	150	170	6.0	0.03	1.8
	Storm	Md.	5.8	0.9	14	0.07	0.8	33	220	160	66	22	0.14	1.4
South River @ Forest Park Road	Base	Md.	2.3	0.1	41	0.18	0.09	2.1	51	110	300	5.0	0.01	1.1
	Storm	Md.	6.9	0.7	41	0.12	0.2	1.9	40	130	110	20	0.01	1.0
South Fork Peachtree Crk @ Johnson Rd.	Base	Md.	1.5	0.2	6.0	0.06	0.1	0.6	48	160	69	4.0	0.01	0.9
	Storm	Md.	5.4	0.4	13	0.15	0.3	1.0	39	120	27	22	0.03	1.2
North Fork Peachtree Crk @ Buford Hwy	Base	Md.	1.4	0.13	7.0	0.06	0.06	0.6	45	120	150	4.0	0.01	0.9
	Storm	Md.	3.3	0.4	20	0.11	0.2	0.9	41	120	49	25	0.01	1.0
Peachtree Creek @ Northside Dr.	Base	Md.	2.1	0.14	7.0	0.06	0.2	0.6	40	180	100	8.0	0.01	1.0
	Storm	Md.	9.3	1.0	32	0.09	0.3	1.4	41	100	31	33	0.03	1.1
Nancy Creek @ Ricken-backer Dr.	Base	Md.	1.4	0.2	6.0	0.4	0.2	0.6	37	130	110	6.0	0.01	0.9
	Storm	Md.	3.1	0.4	7.4	0.07	0.3	0.9	46	120	33	26	0.01	0.9
Nancy Creek @ West Wesley Road	Base	Md.	1.2	0.2	18	0.13	0.10	0.5	34	130	67	5.5	0.01	0.8
	Storm	Md.	4.1	0.4	8.8	0.08	0.28	1.1	36	100	26	22	0.03	1.0
Proctor Creek @ State Road 280	Base	Md.	2.8	0.7	13	0.05	0.09	1.8	52	110	73	6.0	0.07	1.3
	Storm	Md.	11	1.4	24	0.07	0.4	1.9	52	97	26	31	0.09	1.2
North Fork Utoy Creek @ Peyton Rd	Base	Md.	1.4	0.2	6.0	0.1	0.1	0.7	49	120	66	4.5	0.01	1.0
	Storm	Md.	6.7	1.2	25	0.11	0.22	1.5	39	130	68	24	0.04	1.1
Utoy Creek @ Great South-west Pky	Base	Md.	1.4	0.2	84	0.04	0.12	1.0	42	120	250	8.0	0.01	0.8
	Storm	Md.	5.7	0.6	78	0.1	0.23	1.5	41	140	71	27	0.01	1.0
Aquatic criteria[a]	Cont.[b]		9.0	2.5	120	0.25	74	52	N/A	1000	N/A	87	0.03[d]	0.62[d]
	Max.[c]		13	65	120	2.0	570	470	N/A	N/A	N/A	750		

[a] US EPA (2006) National Recommended Water Quality Criteria.

[b] Cont. – continuous exposure

[c] Max. – maximum exposure

[d] Reference level for level III ecoregion 45 streams (US EPA, 2000).

concentrations of sediment-associated constituents (e.g. Horowitz, 1995). Al and Ti are exceptions. The higher stormflow concentrations of these elements may indicate increasing amounts of coarser aluminosilicates (e.g. feldspar, plagioclase) that are suspended and transported during storms, and which also may be acting as diluents for the finer-grained more constituent-rich fractions. The concentrations of the majority of the sediment-associated constituents, whether collected under baseflow or stormflow, are elevated relative to typical background levels. (Table 3(a); e.g. Horowitz *et al.*, 1991; Horowitz, 1995).

On the other hand, median stormflow dissolved concentrations tend to be higher than median baseflow levels (Table 3(b)). At first glance, this may appear surprising because rainwater tends to function as a diluent; a view supported by drops in instream specific conductance (indicative of reduced dissolved solids) at the onset of a storm. However, soon after the "first flush" of rainwater, instream specific conductance rises in conjunction with the dissolved concentrations of a number of constituents. The rise in both conductance and dissolved constituent concentrations probably derives from nonpoint sources as a result of the solubilization of dryfall from impervious surfaces or surface soils (e.g. Ellis, 1999). It also may indicate the discharge of near-surface groundwater due to infiltration (e.g. Ellis, 1999; Shepherd *et al.*, 2006). Several median dissolved concentrations exceed current US Environmental Protection Agency (USEPA) water quality criteria (Table 3(b), USEPA, 2006). Also, a number of the dissolved total P (TP) and total N (TN) levels exceed USEPA recommended levels for Ecoregion 45 (Piedmont) streams (Table 3(b); USEPA, 2000).

An objective of the COA monitoring programme is the calculation of annual fluxes for various sediment-associated and dissolved chemical constituents to evaluate the impact of the city on downstream water quality, as well as to identify water-quality trends. Despite the availability of several measurements from the fully-instrumented sites, no useful surrogates were found for predicting sediment-associated trace element, major element, or nutrient concentrations. The "best" candidate was SSC; however, even the smallest errors associated with this approach averaged ±30–35% over the entire concentration range. When SSC first had to be predicted using site-specific rating curves in lieu of measured values, the average errors increased to about ±90%.

Elsewhere, when limited chemical data could not be supplemented by surrogate-derived predictions, chemical fluxes have been calculated using annual mean/median concentrations derived from actual baseflow and stormflow samples (e.g. Horowitz, 1995; Horowitz *et al.*, 2001). Typically, in these prior cases, constituent concentrations displayed limited interannual variability (usually within, or close to the level of analytical error), 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 is markedly greater, but typically does not exceed a factor of 2. This variability is common in urban areas where there are numerous point and nonpoint sources, and as a result of the chemical impacts of differing periods of antecedent dry conditions on successive storms (Larsen *et al.*, 1999; Shepherd *et al.*, 2006). As a result of the interannual variability among median chemical concentrations, as well as the limited amount of storm sampling (5 or 6 events out of 40 $year^{-1}$), annual chemical flux estimates should be viewed as first approximations only, and subsequent data interpretations for either spatial and/or temporal differences/trends need to be substantial to be considered significant.

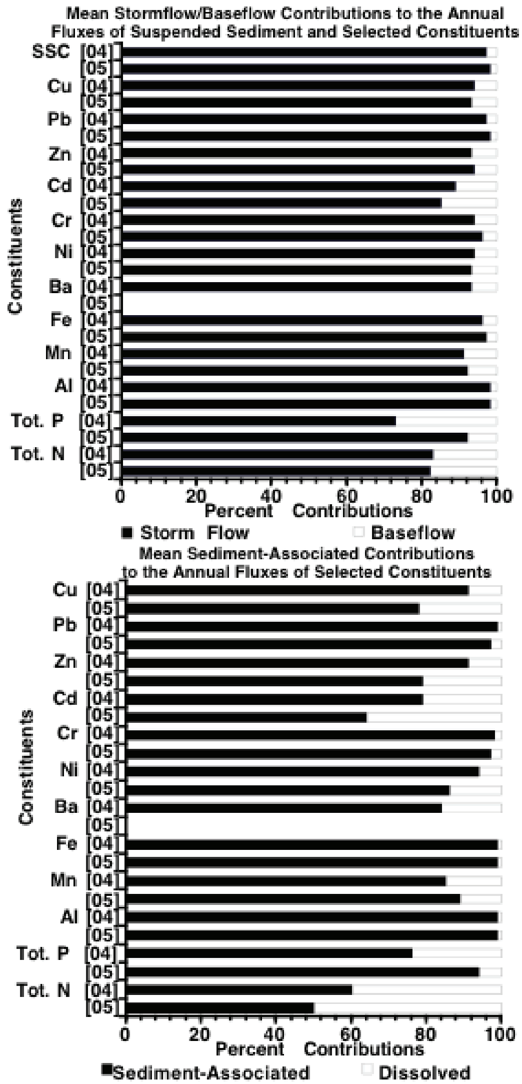

Fig. 4 A summary of the relative importance of stormflow *vs* baseflow, and sediment-associated *vs* dissolved contributions to the annual fluxes of suspended sediment and selected chemical constituents.

With the relatively consistent exception of TN, the majority (≥75%) of the annual fluxes of Cu, Pb, Zn, Cd, Cr, Ni, Ba, Fe, Mn, Al and TP occur in association with suspended sediment (Fig. 4). Further, and again with the exception of TN, ≥90% of the annual fluxes of these same constituents are transported by stormflow (Fig. 4). Although there are exceptions, typically 40–60% of TN occurs in association with suspended sediment, and ≥80% is transported during storms (Fig. 4). These results confirm the view that stormflow, rather than baseflow, and nonpoint rather than point sources, are the major source(s) for the annual fluxes of suspended sediment and various chemical constituents derived from the COA watersheds (e.g. Horowitz *et al.*, 2005). As a result, future efforts will concentrate on better delimiting storm-derived sediment-associated chemical concentrations using automatic samplers to generate composite samples for subsequent chemical analysis.

Impact of the COA on annual fluxes in the Peachtree and Nancy Creek basins

Peachtree (PEA-4, PEA-5, and PEA-2) and Nancy Creeks (NAN-3 and NAN-1) have multiple fully-instrumented sites that permit some assessment of the impact of the COA on downstream water quality, the annual fluxes of suspended sediment, and a variety of chemical constituents (Fig. 1; Table 4). In Nancy Creek, during both 2004 and 2005, more sediment entered the system than was discharged. However, visual observation indicates active, but localized erosion (e.g. streambank undercutting). Hence, it appears that the Nancy Creek watershed represents an area of sediment exchange, resulting in a net decline in sediment loads. Further, it appears that the sediment load in 2005 was less than in 2004 (Table 4). However, this should be viewed with caution because there were substantially greater amounts of missing data during 2005 (Table 4). In 2004, with the exception of TN (which showed an increase), processes within the watershed did not substantially impact the chemical loadings in Nancy Creek. On the other hand, in 2005, these same processes did generate changes in the chemical loadings; Cu, Pb, Fe and TN doubled, whereas Zn and TP quadrupled (Table 4).

In 2004, Peachtree Creek mirrored Nancy Creek, and showed a net decline in suspended sediment loading, along with marginal declines in the fluxes of Mn, TP and TN (Table 4). Once again, these observations should be viewed with caution, because they may have resulted from the greater amount of missing data from the most downstream site relative to the two upstream sites (4.6 *vs* 15 days). On the other hand, in 2005, Peachtree Creek showed a net increase in suspended sediment loading that was accompanied by substantial increases in the fluxes of Cu, Zn, TP and TN. These changes are unlikely to have been caused by missing data because in 2005, the upstream and downstream data losses were roughly equal (Table 4). It should be noted that the impact of the COA on sediment loading in both watersheds would not have been detectable solely on the basis of suspended sediment fluxes; the chemical data provided the key.

Table 4 Downstream changes in the annual fluxes of suspended sediment and selected chemical constituents in Nancy and Peachtree Creeks during 2004 and 2005.

Year	Sites	Rel. loc'n	Discharge ($m^3 \times 10^6$)	SSC (t)	Cu (t)	Pb (t)	Zn (t)	Cd (t)	Cr (t)	Ni (t)	Ba (t)	Fe (t)	Mn (t)	Al (t)	Tot. P (t)	Tot. N (t)	Missing data (days)
Nancy Creek																	
2004	NAN-3	Up	51	25 000	0.9	1.0	5.1	0.01	1.1	0.5	14	810	39	1700	17	96	6.8
	NAN-1	Down	59	18 000	1.1	1.1	5.0	0.01	1.2	0.7	12	770	40	1400	18	130	4.4
2005	NAN-3	Up	51	20 000	0.5	0.4	1.7	0.01	0.5	0.3	*	270	12	820	4.5	60	32.9
	NAN-1	Down	54	16 000	1.1	0.7	6.8	0.01	0.8	0.5	*	580	32	1000	17	110	31.0
Peachtree Creek																	
2004	PEA - 4 + PEA - 5	Up	114	45 000	2.5	2.3	12	0.02	2.2	1.2	25	1 700	73	3 600	58	270	4.6
	PEA - 2	Down	136	36 000	2.4	2.4	11	0.03	2.0	0.9	26	1 500	58	3 300	43	250	15.0
2005	PEA - 4 + PEA - 5	Up	125	43 000	2.5	2.1	13	0.03	2.2	1.1	*	1 600	76	3 100	36	240	18.0
	PEA - 2	Down	161	48 000	3.9	3.1	18	0.03	2.6	1.2	*	1 800	77	3 600	57	430	19.8

* Dissolved Ba data were only generated in 2004.

CONCLUSIONS

(1) Accurate flux estimates in the relatively "flashy" COA urban streams require shorter time-step calculations than in larger systems; at a minimum, based on the potential errors associated with measuring discharge and SSC, the time steps may have to be on the order of 2–3 h.
(2) During 2004 and 2005, the COA watersheds discharged some 150 000 t of suspended sediment; ≥94% of the transport occurred in conjunction with stormflow, which also accounted for ≥65% of the annual discharge, and occurred for time periods amounting to ≤20% of the year.
(3) The annual median chemical concentrations of sediment-associated constituents tend to be higher during baseflow than stormflow, but in either case, are elevated compared to background.
(4) On the other hand, the chemical concentrations of dissolved constituents tend to be higher during stormflow than baseflow; a number of these concentrations exceed USEPA water quality criteria (trace/major elements) and/or recommendations (nutrients).
(5) Based on annual median chemical concentrations for baseflow and stormflow, with the exception of TN, the annual fluxes of ≥75% of trace elements, major elements and TP occurred in association with suspended sediment; in turn, ≥90% of the transport of these same constituents occurred in conjunction with stormflow.
(6) Sediment-associated TN fluxes range from 50 to 60% of the annual total; even so, storm-related transport typically exceeds 80% of the annual load.
(7) Annual baseflow suspended sediment and sediment-associated, and baseflow and stormflow dissolved chemical fluxes were relatively insignificant compared to the fluxes of storm-derived suspended sediment and sediment-associated chemical fluxes.
(8) The majority of suspended sediment and sediment-associated chemical fluxes in the COA appear to be derived from nonpoint rather than point sources.

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