HYDROLOGICAL PROCESSES
Hydrol. Process. **23**, 2860–2878 (2009)
Published online 13 August 2009 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/hyp.7373

Effects of urbanization on stream water quality in the city of Atlanta, Georgia, USA†

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Abstract:

A long-term stream water quality monitoring network was established in the city of Atlanta, Georgia during 2003 to assess baseline water quality conditions and the effects of urbanization on stream water quality. Routine hydrologically based manual stream sampling, including several concurrent manual point and equal width increment sampling, was conducted ∼12 times annually at 21 stations, with drainage areas ranging from 3·7 to 232 km^2. Eleven of the stations are real-time (RT) stations having continuous measures of stream stage/discharge, pH, dissolved oxygen, specific conductance, water temperature and turbidity, and automatic samplers for stormwater collection. Samples were analyzed for field parameters, and a broad suite of water quality and sediment-related constituents. Field parameters and concentrations of major ions, metals, nutrient species and coliform bacteria among stations were evaluated and with respect to watershed characteristics and plausible sources from 2003 through September 2007. Most constituent concentrations are much higher than nearby reference streams. Concentrations are statistically different among stations for several constituents, despite high variability both within and among stations. Routine manual sampling, automatic sampling during stormflows and RT water quality monitoring provided sufficient information about urban stream water quality variability to evaluate causes of water quality differences among streams. Fecal coliform bacteria concentrations of most samples exceeded Georgia's water quality standard for any water-usage class. High chloride concentrations occur at three stations and are hypothesized to be associated with discharges of chlorinated combined sewer overflows, drainage of swimming pool(s) and dissolution and transport during rainstorms of $CaCl_2$, a deicing salt applied to roads during winter storms. One stream was affected by dissolution and transport of ammonium alum [$NH_4Al(SO_4)_2$] from an alum-manufacturing plant; streamwater has low pH (<5), low alkalinity and high metals concentrations. Several trace metals exceed acute and chronic water quality standards and high concentrations are attributed to washoff from impervious surfaces. Published in 2009 by John Wiley & Sons, Ltd.

KEY WORDS urbanization; stream water quality; nutrients; bacteria; major ions; weathering; monitoring

Received 20 October 2008; Accepted 7 May 2009

INTRODUCTION

Human activities have the potential to cause changes to the environment. Alteration of the land surface for various uses including light and heavy industry, urbanization and suburban development has changed water pathways and induced changes to natural processes (Booth and Jackson, 1997; Poff *et al.*, 1997). Human activities can be sources of elements and compounds to the landscape and receiving waters through various pathways, including atmospheric deposition, solid and liquid waste disposal and a combination of diffuse and point-source distribution (Peters and Meybeck, 2000). In addition, types of contaminants and mechanisms for waste disposal vary with time, economy, technology and culture. Resource management has targeted environmental improvement resulting from the understanding of deleterious effects of various elements and compounds on the environment (Peters, 2008). A major deficiency in evaluating stream water quality is that there are no detailed records of the temporal and spatial variations in waste disposal and other sources of solutes to streams. For example, little data exist for factors such as construction-caused changes, alteration of hydrological pathways and solute transport along those pathways.

Many studies have been conducted to assess urban stream water quality (Driver and Troutman, 1989; Makepeace *et al.*, 1995; Mulliss *et al.*, 1996; Deletic, 1998; Duda *et al.*, 1998; Ellis, 2004; Carle *et al.*, 2005; Soller *et al.*, 2005; Brilly *et al.*, 2006; Hudak and Banks, 2006). These studies indicate elevated but highly variable concentrations of most constituents in urban streams, with several constituents exceeding public health standards. Other urban runoff studies focused on the water quality during storms of specific hydrologic pathways including temporal characteristics, such as first flush of solutes, to assess the cause of elevated concentrations in urban streams. For example, metal concentrations and partitioning between dissolved and particulate phases from various sources including roads, parking lots, roofs and atmospheric deposition (Lara-Cazenave *et al.*, 1994a,b; Sansalone and Buchberger, 1997; Gromaire-Mertz *et al.*, 1999; Davis *et al.*, 2001; Mosley and Peake, 2001; Gnecco *et al.*, 2005; Lee *et al.*, 2005; Sansalone *et al.*, 2005; Brown and Peake, 2006), bacteria concentrations

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in non-point and point source runoff (Duda *et al*., 1998; Ellis, 2004; O'Keefe *et al*., 2005; Garcia-Armisen and Servais, 2007), water quality of combined sewer systems (Gupta and Saul, 1996; Barco *et al*., 2008) and water quality of runoff from golf courses (Mallin and Wheeler, 2000).

The study herein focuses on stream water quality of the Atlanta region. Previous studies in the region provided some background on anticipated water quality characteristics. Rose (2007) assessed the impacts of urbanization on base flow hydrochemistry of the Chattahoochee River Basin from a synoptic sampling of 35 streams during April and May 2005. The study results indicate that urbanized watersheds were associated with higher concentrations of sulfate, chloride, alkalinity (ALK), potassium and sodium than rural watersheds. Furthermore, a high correlation between urbanization and sodium-potassium-chloride concentrations was attributed to a widespread input of electrolytes present in human waste and wastewater.

A study with similar but more extensive data collection in the Atlanta region than that of the Rose (2007) study was conducted by Gregory and Calhoun (2007) during the 2003 water year (WY2003, 1 October, 2002, through 30 September, 2003). Water samples were collected during spring and summer base flow at 30 stations and bimonthly at 10 of the 30 stations for nutrients, pesticides, chloride, sulfate, dissolved and particulate organic carbon, particulate nitrogen, suspended sediment (SS), turbidity (TURB) and *Escherichia coli* (EC). In addition, hydrology, stream habitat and algal, macroinvertebrate and fish communities were evaluated. Gregory and Calhoun (2007) reported that specific conductance (SC) and concentrations of chloride, sulfate and pesticides increased as urbanization increased. However, nutrient concentrations did not correlate with urbanization, but negatively correlated with percentage forest cover of the watersheds. Even with this relatively short study period, Gregory and Calhoun (2007) reported statistically significant relations between urbanization and flashiness of hydrographs and shorter periods of high flow.

Stormflow was also reported to be flashy in urban watersheds compared with agricultural or forested watersheds in the West Georgia Piedmont by Schoonover *et al*. (2006). These results are consistent with hydrologic analysis of seven north Georgia watersheds for a 38-year period of record, including a highly urbanized Atlanta watershed, by Rose and Peters (2001). In addition to increased flashiness associated with urbanization, the base flow recession constant (a measure of the rate at which groundwater is released from storage to the stream as base flow from May to September) and base flow were much less than for rural streams. Rose and Peters (2001) also reported a decrease in groundwater levels for wells concurrent with increasing urbanization and hypothesized that the decrease was caused by decreased groundwater recharge in the urban watersheds due to increased imperviousness and related rapid storm runoff.

The water quality studies of watersheds of the Atlanta region by Rose (2007) and Gregory and Calhoun (2007) targeted chronic water quality conditions, i.e. during base flow. The studies also included watersheds that covered a broad range of land use from rural to highly urban. The results clearly indicate effects of urbanization on water quality during base flow, but did not show water quality *among* highly urbanized watersheds over a large streamflow range.

Finally, Rose *et al*. (2001) evaluated dissolved trace metal concentrations during 1998 and 1999 of streams in the Atlanta region. Rose *et al*. (2001) also sampled urban street, suburban street and parking lot runoff. The highest zinc concentrations were collected from an urban street runoff having median concentrations 2 orders of magnitude higher than base flow from non-urban streams. Zinc concentration in urban stream stormflow was higher than base flow and each was higher than non-urban stream base flow. Rose *et al*. (2001) analyzed concentration hysteresis during storms of several urban streams and assessed a zinc mass balance, concluding that much of the zinc mobilized during storms, i.e. from impervious traffic areas, is lost and likely adsorbed to sediment.

The objectives of this study are the following: (1) to determine the baseline water quality characteristics of city of Atlanta (COA) streams over a wide discharge range; (2) to evaluate water quality differences among COA sampling stations with respect to field parameters and concentrations of major ions, minor and trace metals, nutrients and bacteria; (3) to compare COA stream water quality for a subset of parameters to those at nearby reference stations including a small (0·4 km^2) relatively undisturbed forested watershed and a larger (10 km^2) low-density residential watershed; and (4) to evaluate some of the water quality differences among and within COA sampling stations with respect to land-use characteristics and other environmental factors including streamflow as a means of identifying potential causes of impairment. Even in the best case where sources are clearly defined, it is problematic to quantitatively link source contributions to stream water quality. However, the data analysis of stream water quality variability using three types of monitoring approaches identified some major differences among streams, which indicated links to primary causative factors.

Study area characteristics and stream water quality monitoring program

The COA encompasses 343 km^2 and is approximately centred within the ten-county Atlanta Regional Commission (ARC) planning area (4780 km^2). All but four of the Long-Term Watershed Monitoring Program (LTWMP) sampling stations are within the COA boundary (Figure 1). The average elevation of the COA is 320 m (NAD27), which is the highest average elevation of any major city east of Denver. The northern and western parts of COA drain to the Chattahoochee River, which drains to the Gulf of Mexico. The southeastern part

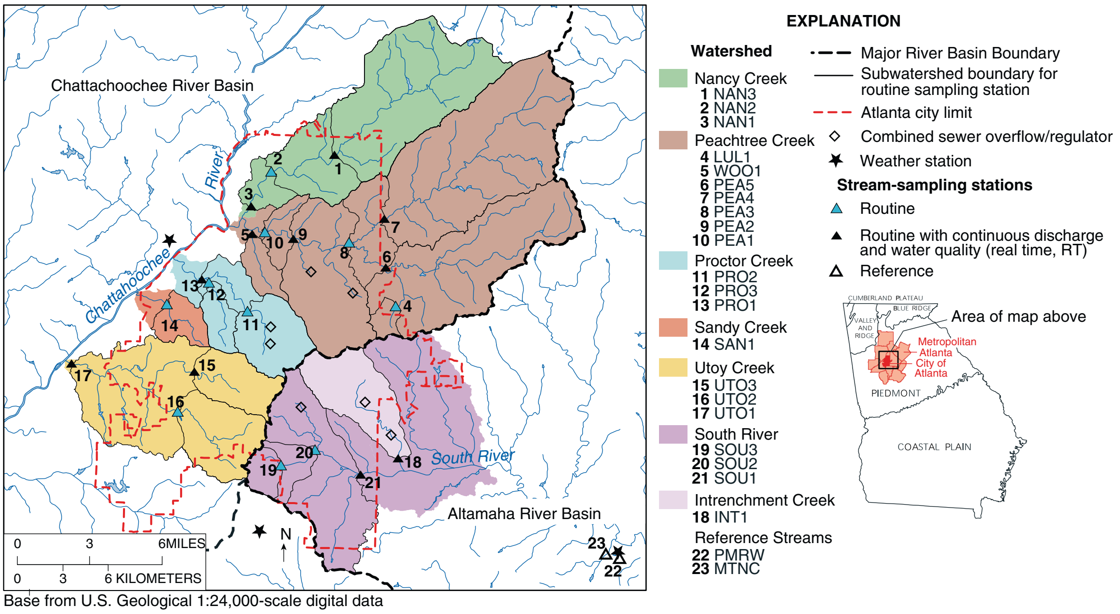

Figure 1. City of Atlanta, Georgia (USA) and reference stream monitoring stations

of COA drains to the South River and subsequently to the Ocmulgee River, which drains to the Atlantic Ocean (Figure 1; Table I).

Urbanized areas, forest and agriculture are the dominant land use and land cover in the Atlanta region, which is undergoing rapid development and population growth. Atlanta has been one of the fastest growing metropolitan area in the nation. The ten-county Atlanta metropolitan area is a sprawling urbanized and sub-urbanized complex in which the population has increased from 1·5 million in 1970 to 4·1 million people in 2008 with a 19·5% population increase from 2000 to 2008 (ARC, 2008). Most of the population increase has been in the counties around the COA, but population density also is very high in COA with an average of 1510 people km^{-2}. Urban land use in the COA watersheds ranges from 69 to 96% (Table II), and most of the remaining land use is either low-density residential or forest (ARC, 2004).

The COA is in the Piedmont physiographic province and is underlain by medium- to high-grade metamorphic and igneous rocks (Higgins and Crawford, 2006). On average, the study area receives 1340 mm precipitation annually, generally distributed uniformly during the year, at least with respect to monthly totals (Rose and Peters, 2001). From April through October, rainstorms are primarily convective (high intensity and short duration), with intermittent occurrence through November and beginning in March. During the remainder of the year, precipitation is dominated by synoptic-scale weather systems (low intensity and long duration). The runoff coefficient (RC; runoff as a percentage of precipitation) of suburban to urban watersheds ranges from approximately 30 to 40%; the highest RCs are in watersheds with the highest percentages of impervious area (Rose and Peters, 2001). Stream base flow varies seasonally; the lowest flow occurs during the summer growing season when evapotranspiration is the highest and the highest base flow occurs during the winter dormant season. Furthermore, the distribution of hourly streamflow at a long-term gauging station, which was one of the COA stream stations (PEA2), was evaluated during the design of the LTWMP (Figure 2). The distribution of hourly streamflow indicates that stormflow is flashy with very short times to peak (Rose and Peters, 2001) and that major storms typically occur during non-working hours from 16 : 00 through the night until about 6 : 00. Figure 2 also indicates that stormflows during summer are almost entirely affected by convective storms, and most of the highest stormflows occur during nighttime.

METHODS

The Clean Water Atlanta Program developed a LTWMP in December 2002 (Horowitz and Hughes, 2006; Horowitz *et al.*, 2007; COA, 2009) and the US Geological Survey (USGS) initiated stream water quality sampling during 2003. The LTWMP consists of a network of 21 regularly sampled stream stations with watersheds ranging in size from 3·7 to 232 km^2. For station locations and station name designation, see Figure 1 and Table I. The analyses include the following: (1) field parameters (temperature [T], SC, pH, dissolved oxygen [DO] and TURB); (2) major ions (calcium [Ca], magnesium [Mg], sodium [N], potassium [K], chloride [Cl], sulfate [SO_4], silica [SiO_2] and ALK); (3) nutrients (ammonium [NH_4N], nitrite [NO_2N], nitrate [NO_3N], phosphate [PO_4P] and total phosphorus [TP]); (4) indicator coliform bacteria (fecal coliform [FC], total coliform [TC] and EC, reported as most probable number (MPN) of colonies dl^{-1}); (5) minor and trace metals (aluminum [Al], copper [Cu], cadmium [Cd], hexavalent chromium [Cr], iron [Fe], lead [Pb], manganese [Mn] and zinc [Zn]); and SS. Laboratory analytical detection limits and method report

Table I. City of Atlanta and reference stream water quality monitoring stations, Georgia

Major river basin	Stream watershed	Station designation	US Geological Survey station number	Stream name and station location	Drainage area (km^2)	Elevation (m above sea level)			Relief (m)
						Average	Minimum	Maximum	
Chattahoochee	Nancy Creek	NAN3	02 336 360	Nancy Creek at Rickenbacker Drive.	67·1	293·5	235·4	352·5	117·1
Chattahoochee	Nancy Creek	NAN2	02 336 380	Nancy Creek at Randall Mill Road	88·2	293·5	235·4	352·5	117·1
Chattahoochee	Nancy Creek	NAN1	02 336 410	Nancy Creek at West Wesley Road	95·4	291·1	229·8	352·5	122·7
Chattahoochee	Peachtree Creek	LUL1	02 336 228	Lullwater Creek at Lullwater Parkway	3·7	295·8	269·8	319·3	49·4
Chattahoochee	Peachtree Creek	WOO1	02 336 313	Woodall Creek at DeForrs Ferry Road	6·7	266·9	235·1	302·6	67·6
Chattahoochee	Peachtree Creek	PEA5	02 336 240	South Fork Peachtree Creek, Johnson Road	70·8	299·3	246·7	341·1	94·4
Chattahoochee	Peachtree Creek	PEA4	02 336 120	North Fork Peachtree Creek, Buford Highway	90·2	293·1	245·5	341·6	96·1
Chattahoochee	Peachtree Creek	PEA3	02 336 267	Peachtree Creek at Piedmont Road	176·9	293·6	240·6	341·9	101·3
Chattahoochee	Peachtree Creek	PEA2	02 336 300	Peachtree Creek at Northside Drive	220·5	290·5	232·7	341·9	109·2
Chattahoochee	Peachtree Creek	PEA1	02 336 311	Peachtree Creek at Bohler Road	227·7	289·6	228·9	341·9	113·0
Chattahoochee	Peachtree Creek	PRO2	02 336 517	Proctor Creek at Hortense Way	19·8	290·9	230·3	323·6	93·3
Chattahoochee	Peachtree Creek	PRO3	0 23 365 218	Proctor Creek Trib at Spring Road	7·8	278·7	235·3	322·1	86·8
Chattahoochee	Peachtree Creek	PRO1	02 336 526	Proctor Creek at Jackson Parkway	36·2	282·2	252·7	323·6	69·9
Chattahoochee	Sandy Creek	SAN1	02 336 644	Sandy Creek at Bolton Road	8·8	269·6	236·1	301·0	64·9
Chattahoochee	Utoy Creek	UTO3	02 336 658	North Utoy Creek at Peyton Road	17·2	297·0	253·1	321·8	68·7
Chattahoochee	Utoy Creek	UTO2	02 336 706	South Utoy Creek at Childress Drive	24·	289·7	244·7	324·7	79·9
Chattahoochee	Utoy Creek	UTO1	02 336 728	Utoy Creek at Great Southwest Parkway	89·	277·2	224·9	324·7	99·7
Ocmulgee	South River	INT1	02 203 700	Intrenchment Creek at Constitution Avenue	27·4	288·8	234·8	320·5	85·7
Ocmulgee	South River	SOU3	02 203 603	South River at Springdale Road	6·1	297·9	259·0	323·1	64·1
Ocmulgee	South River	SOU2	02 203 620	South River at Macon Drive	13·5	289·3	246·3	323·1	76·8
Ocmulgee	South River	SOU1	02 203 655	South River at Forest Park Road	58·8	283·1	237·2	323·1	85·9
Ocmulgee	South River	PMRW	02 203 970	Mountain Creek Tributary at Panola Mountain State Park	0·4		224	279	55
Ocmulgee	South River	MTNC	02 2039 675	Mountain Creek near Panola Mountain State Park	10·		210·3		

DOI: 10.1002/hyp

Table II. Percentage land use of basin area for city of Atlanta stream water quality monitoring stations (derived from Atlanta Regional Commission, 2004)

Land-use type	Watershed																				
	Nancy Creek			Peachtree Creek							Proctor Creek			Sandy Creek	Utoy Creek			South River			
	NAN1	NAN2	NAN3	LUL1	PEA4	PEA5	PEA3	PEA2	PEA1	WOO1	PRO2	PRO3	PRO1	SAN1	UTO3	UTO2	UTO1	SOU3	SOU2	SOU1	INT1
Urban																					
Commercial	14·5	15·4	16·9	8·6	14·7	10·7	12·9	14·8	14·5	1·6	13·5	6·6	9·3	6·5	5·3	6·3	4·5	12·2	16·6	11·8	14·5
Industrial and commercial	1·1	1·1	1·5	0	7·2	6·8	6·9	6·8	6·6	52·8	12·2	0	7·5	0	3·5	3·2	4·8	11·1	9·4	12·1	6·2
Industrial	2·2	2·4	3·1	0	0·8	0	0·4	0·6	0·5	0	0	0	0·2	0	0·1	0	0·2	12·9	6·7	1·7	2·1
Institutional, extensive	0·9	1·0	1·3	0	1·4	4·4	2·5	2	1·9	0	0	1·9	2	0	4·2	7·9	4·0	0	0	0	0
Institutional, intensive	4·2	3·3	3·9	0·6	2·6	3·2	2·7	3·5	3·5	0	9·4	4·2	6·9	3·6	0·8	1·6	1·2	5·7	3·5	3·5	5·1
Limited access highway	2·9	2·7	3·2	0	3·1	1·9	2·7	2·8	2·9	0	0·9	1·6	0·8	10·4	0·6	1·4	1·5	0·5	6·8	4·0	3·4
Residential, medium density	52·4	54·0	50·8	26·6	52·7	47·8	49·7	45·9	46·7	5·0	25·9	60·	32·5	60·2	27·7	52·4	39·0	9·8	18·8	21·4	26·6
Residential, high density	0·9	1·0	1·3	41	0	5·4	3·3	4·8	4·6	0	21·5	0	11·9	0	31·9	2·1	6·7	31·6	23·1	16·4	13·4
Residential, mobile homes	0	0	0	0	0	0	0	0	0	0·7	0	0	0	0·7	0	0	0	1·0	0·7	0·3	0
Residential, multi-unit	7	7·3	8	5·7	10·9	7·7	10	9·5	9·6	4·3	5·2	5·6	5·1	3·7	1·1	7·6	4·6	6·3	4·9	4·4	5·2
Transitional	0·6	0·7	0·9	0	0·1	0·4	0·3	0·5	0·5	0·7	0·5	0	2·3	0	0	0·4	0·9	0·8	0·4	1·5	0·7
Transportation	0·9	1	1·3	1·3	2·1	0·6	1·4	1·2	1·2	14·1	1·9	0	5·6	0·3	0·4	1·2	0·8	2·4	1·4	1·0	1·8
Urban, other	0·4	0·4	0·5	4·6	0·6	0·3	0·6	0·8	0·8	4·4	3·4	0	2·4	1·8	0·1	1·4	0·8	0	0	1·2	9·6
Urban subtotal	88·0	90·0	92·6	88·3	96·2	89·2	93·3	93·3	93·3	82·9	84·5	79·8	86·4	87·2	75·6	85·4	69·0	94·4	92·3	79·3	88·5

DOI: 10.1002/hyp

Table II. (*Continued*)

Land-use type	Watershed																				
	Nancy Creek			Peachtree Creek							Proctor Creek			Sandy Creek	Utoy Creek			South River			
	NAN1	NAN2	NAN3	LUL1	PEA4	PEA5	PEA3	PEA2	PEA1	WOO1	PRO2	PRO3	PRO1	SAN1	UTO3	UTO2	UTO1	SOU3	SOU2	SOU1	INT1
Other																					
Agricultural	0·4	0·5	0	0	0	0·2	0·1	0·1	0·1	0	0	0	0	0	0	0	0	0	0	0·1	0
Cemetery	0	0	0	0	0	0·8	0·3	0·3	0·3	7·3	0	7·5	1·8	0	11·9	0·4	2·4	0	0·4	0·4	0·9
Forest	2·9	2·8	3·3	2·0	2·4	5·6	3·9	3·5	3·4	8·9	3·1	10·6	8·7	9·9	9·5	9·7	20·0	5·1	6·6	15·1	7·9
Golf courses	1·4	1·5	2	7·2	0	0·9	0·4	0·4	0·5	0	0	0	0	0	0	1·6	0·4	0	0	1·2	0
Parkland, extensive	1·1	1·2	0	2·6	0·8	1·6	1·0	1·4	1·5	0	0	0	0·8	2·4	2·6	2·0	2·5	0	0	1·7	0
Parks	0·7	0·7	1·0	0	0·3	0·2	0·2	0·3	0·3	0	1·2	2·1	1·1	0·5	0·4	0·7	0·5	0	0	0·9	1·9
Quarries	0	0	0	0	0	0	0	0	0	0·3	1·1	0	1·3	0	0	0	0	0	0	0	0
Reservoirs	0·3	0·3	0·4	0	0·2	0	0·1	0·2	0·2	0	0	0	0	0	0	0	0·4	0	0	0·1	0·2
Residential, low density	5·1	2·7	0·7	0	0	1·2	0·5	0·4	0·4	0	0	0	0	0	0	0·3	4·5	0·5	0·8	0·7	0·7
Wetland	0·0	0·1	0·1	0	0·1	0·2	0·1	0·1	0·1	0	0	0	0	0	0	0	0·3	0	0	0·6	0
Watershed area (km^2)	95·4	88·2	67·1	3·7	90·2	70·8	176·9	220·5	227·7	6·7	19·8	7·8	36·2	8·8	17·2	24	89	6·1	13·5	58·8	27·4

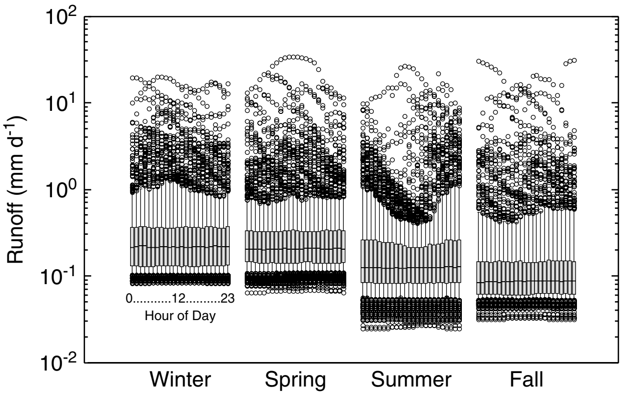

Figure 2. Seasonal distribution of hourly discharge for a 5 year period of record at PEA2 from 1997 to 2001, i.e., prior to initiation of the COA stream water quality sampling. Seasons are consecutive three month periods and Winter includes December, January, and February

limits have improved (are lower) for most nutrient species since the study began. Also, FC analyses were ceased beginning in March 2007 because of program changes. Eleven of the sampling stations were instrumented with real-time (RT) water quality monitors for field parameters (T, SC, pH, DO and TURB) using standard USGS procedures for operating and maintaining continuous water quality monitors (Wagner *et al.*, 2006). These 11 stations also were instrumented with continuous stage monitors for estimating discharge (Q) using standard USGS procedures for measuring and computing discharge (Rantz, 1982). Ten RT stations were instrumented during 2003. Station WOO1 was instrumented in June 2005; UTO3 was deactivated at the end of 2006; and the RT equipment moved from UTO3 to SOU3 (only UTO3 shown as RT station on Figure 1). Sampling consisted of equal width increment (EWI) and manual point or grab (GRAB) sampling at each station (USGS, variously dated) and automated Teledyne ISCO Model 6712FR refrigerated pump sampling (ISCO) from a point intake at the RT stations for stormflow sampling.

Most stations were manually sampled at least 30 times since the study began and most of the RT stations were automatically sampled more than 150 times. The samples were processed and preserved using standard USGS water quality field sampling protocols (USGS, variously dated) and submitted to USGS laboratories for analyses following techniques and procedures described by Fishman and Friedman (1989). To monitor stream outflow from the COA, seven stations (NAN1, PEA1, PRO1, SAN1, UTO1, INT1 and SOU1) are located at the most downstream location of the seven study watersheds (Figure 1, Table I). To monitor stream inflow to the COA, three stations (NAN3, PEA4 and PEA5) are located at the most upstream location near the COA boundary; these tributary streams have substantial drainage areas outside the city limits (Figure 1).

Two nearby stations within the South River Basin to the southeast and outside the COA were used as references for COA water quality (Figure 1, Table I). One reference station, Mountain Creek Tributary in the Panola Mountain Research Watershed (PMRW), is in a small (0·41 km^2), relatively undisturbed, forested watershed in the Panola Mountain State Conservation Park, which has been monitored since 1985. The other reference station, Mountain Creek (MTNC), is in a larger (10 km^2) low-density residential watershed, which has been monitored since 1991. Stream sampling was conducted weekly, and in PMRW, automatic sampling augmented the weekly manual grab sampling during rainstorms, similar to the RT COA stations. For the reference stations, water quality sampling and sample processing differed from those of the COA streams. At PMRW and MTNC, the manual (GRAB) samples were collected at a point and at PMRW, the automatic samples (ISCO) were collected at the end of the sampler tubing located in the pool above the weir plate. Samples were not filtered, but were chilled after retrieval during transport and then stored in a refrigerator prior to analysis. The concentrations of the major ions and nutrients at PMRW were compared among filtered (0·1 and 0·45 μm) and non-filtered samples during the first couple of years of the study (1985–1986) and no statistically significant differences were detected among them. The laboratory analytical procedures were the same as those used for the COA samples. Some of the COA water quality parameters were not analyzed at the reference stations, as noted by the absence of data for these stations in the Results and Discussion.

RESULTS AND DISCUSSION

Many water quality data were collected from COA streams. The results and discussion have been organized to help simplify and focus the presentation. The hydrologic characteristics are presented first, which is followed by the stream water quality. General characteristics of the stream water quality are compared among stations, and to do this, the water quality constituents are separated into groups including major ions, nutrients, bacteria and DO and metals. Where differences among stations occur for a constituent or group of constituents, other constituents are included as the combination of behaviours alludes to process or cause and effect. The last section on water quality addresses the general effects of streamflow on water quality and does not address groups of constituents *per se*.

Rainfall and runoff characteristics

Three long-term weather stations are located in or near the COA (Figure 1). Two of the stations are operated by the National Weather Service (NWS). One NWS station with continuous data since WY1931 is located to the south at Atlanta Hartsfield-Jackson International Airport and the other NWS station (Atlanta-Bolton) with generally continuous data since WY1957 is located to the west of COA (http://www7.ncdc.noaa.gov/CDO/cdo). The third station with continuous data since WY1986 is at the PMRW, southeast of the COA (Figure 1). The long-term average WY precipitation ranged from 1240 mm in the southeast to 1360 mm in the northwest. During the study, precipitation was highest during WY2005 with each station reporting approximately 1600 mm, and lowest during WY2007 with a range from 850 to 950 mm from southeast to northwest. Precipitation at the three weather stations averaged 1300, 1600, 1270 and 890 mm for WY2004, WY2005, WY2006 and WY2007, respectively.

The annual RC (runoff/precipitation) of the 10 long-term RT stations averaged 0·43, 0·51, 0·35 and 0·32 for WY2004–2007, respectively. In contrast, the RC for forested PMRW reference station was 0·27, 0·40, 0·30 and 0·25, which is generally consistent with the inter-annual COA results. The urban streams generated more runoff than the reference watershed; COA RCs are higher than PMRW RCs, which also is consistent with the results reported by Rose and Peters (2001). High RCs at the COA stations are attributed to more impervious area, artificial channels and conveyances in the urbanized streams, which are more effective at transferring water to COA streams than natural infiltration through soils followed by groundwater discharge to the streams.

Stream water quality variations among stations

Water quality also varied markedly within and among stations. The distribution of concentrations of SO_4, nutrients, bacteria and metals at both COA and reference stations was positively skewed, i.e. asymmetrical with most values clustered at the lower end of the scale (Figures 3), which has been reported elsewhere for most of these constituents (van Buren *et al*., 1997). Urbanization has a marked effect on water quality. The concentrations of most constituents at each station were statistically significantly higher than those of the two reference stations. Also, ISCO sampling at the RT stations provided a much more thorough characterization of the chemical conditions of streamwater during stormflow than at stations where only manual samples were collected; differences

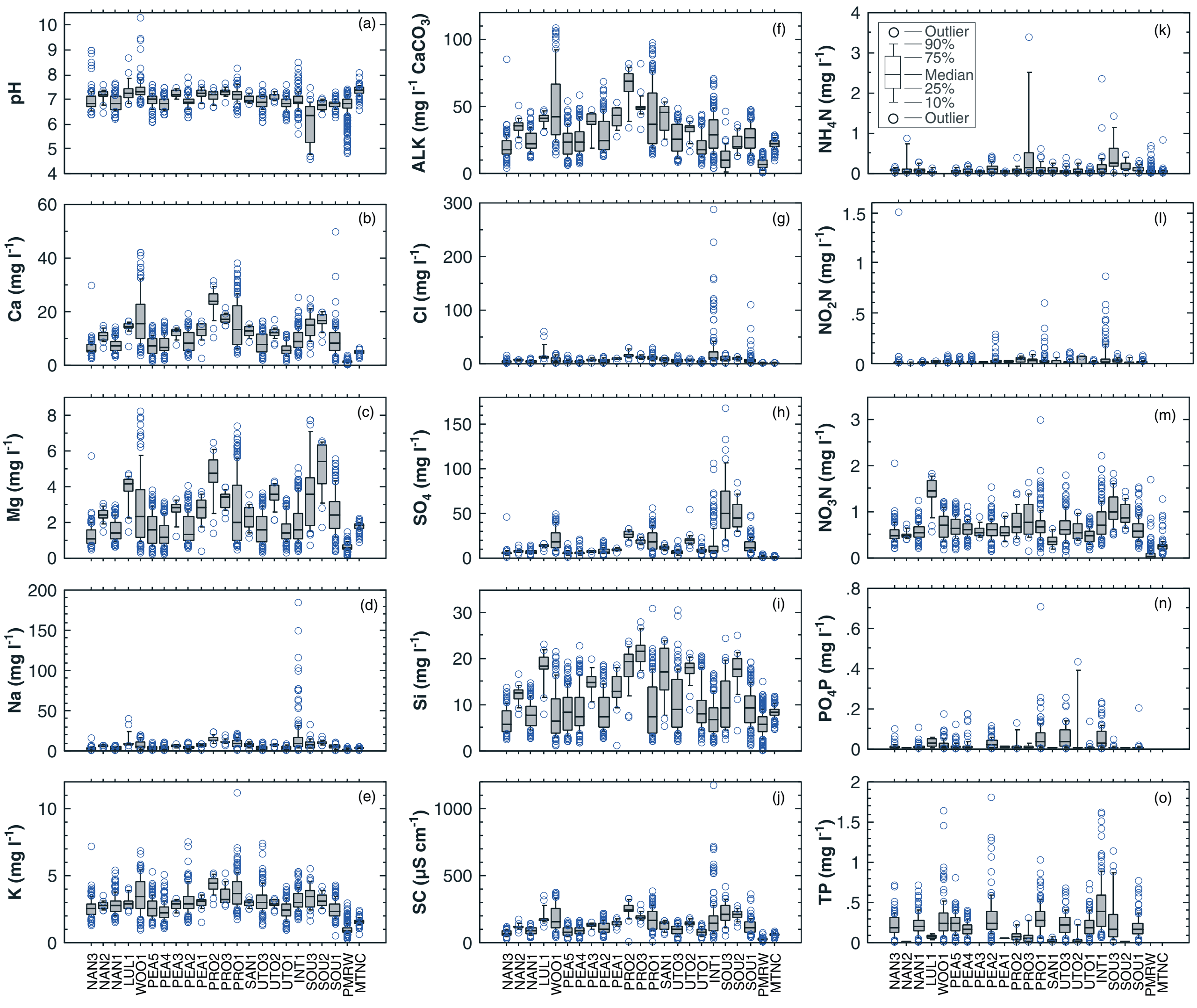

Figure 3. Concentration distributions of (a) pH, (b) Ca, (c) Mg, (d) Na, (e) K, (f) ALK, (g) Cl, (h) SO_4, (i) Si, (j) SC, (k) NH_4N, (l) NO_2N, (m) NO_3N, (n) PO_4P, (o) TP, (p) Al, (q) Mn, (r) Fe, (s) DO, (t) DO Saturation, (u) Cd, (v) Cr, (w) Cu, (x) Pb, (y) Zn, (z) FC, (aa) EC, (ab) TC, (ac) TURB, and (ad) SS for all water quality samples of streams in the city of Atlanta and two reference streams, WY2004–WY2007. The chronic and acute standards for Cd, Cu, Pb and Zn shown on the figure the values for a sample with a hardness of 50 mg l^{-1} as $CaCO_3$; the actual number of samples that exceed the computed standard from the sample hardness is listed in Table III

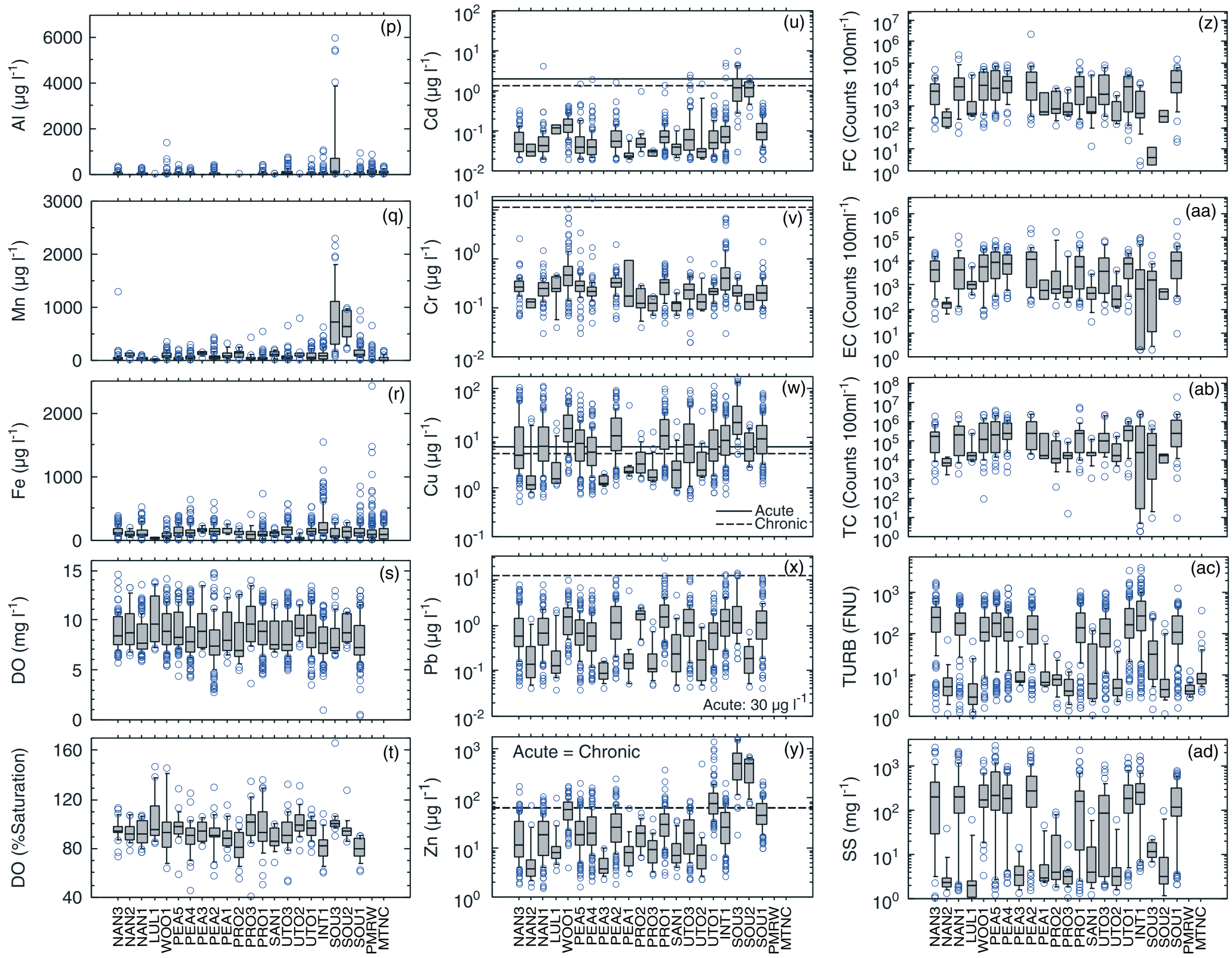

Figure 3. (*Continued*)

were most pronounced when concentrations increased with increasing streamflow.

Concentrations of many constituents can vary spatially in a stream cross-section, particularly large streams and rivers, which could affect interpretation of results generated from point sampling compared with an integrated sample of the cross-section. The concentration variations for EWI and GRAB sampling were evaluated for paired samplings of the COA stations, which were collected over a wide range of streamflows, and results indicate that there is no statistically significant concentration difference between EWI and GRAB sampling for the constituents analyzed herein; this result also was reported for total SS, total dissolved solids, dissolved nutrients and total metals in streamwater of a nearby county (Knaak and Ankcorn, 2003).

Major ions. In general, SC and major ion concentrations varied markedly within samples from a single station. The SC and major ion concentrations also were higher and more variable than those of the two reference stations, despite the low-density residential development of MTNC. On average, SC, Ca, Mg, Na, K, ALK and Si concentrations are 5, 8, 4, 4, 4, 10 and 2 times, respectively, higher at the COA stations than at the PMRW reference station; concentrations at MTNC were, on average, two times higher than at PMRW except for Si, which is comparable; for some constituents such as SO_4, average concentrations at some COA stations were more than 30 times average PMRW concentrations. At each RT station and PMRW, concentrations of most of major ions were highly correlated with each other and negatively correlated with discharge (Spearman rho; $p < 0{\cdot}0001$), with a few exceptions.

Major ion concentrations in natural systems are primarily controlled by weathering and the residence time of water along hydrologic pathways, which provides contact with the soils and rocks in the drainage basin (Drever, 1997). Concentrations of weathering products in groundwater typically increase with residence time. The primary natural weathering process involves H_2CO_3 breakdown of minerals producing base cations (Ca, Mg, Na and K), ALK (primarily bicarbonate) and Si. The concentrations among these major ions at COA stations and PMRW were highly linearly correlated and regression slope differences likely reflect variations in mineralogy of the bedrock and soils. For the COA RT stations and PMRW, the negative correlation of major ion/field property concentrations with discharge is attributed to the dilution of more concentrated long-residence time groundwater, which dominates streamflow during base flow.

The relation between ALK and Si for the stations is quite revealing (Figure 4). Differences in the relation between ALK and Si among stations can reflect the relative contributions of carbonate and aluminosilicate mineral weathering; carbonate mineral weathering produces ALK only, whereas aluminosilicate mineral weathering produces both ALK and Si. Furthermore, carbonate minerals tend to weather faster than aluminosilicate minerals, producing ∼10 times more Ca and ALK in streamwater (Meybeck, 1994). Linear regression relations of ALK on Si for most COA streams were highly significant ($p < 0{\cdot}0001$) and the slopes were approximately 2, except for PRO1, PRO2 and WOO1, which were larger (3·3, 2·5 and 4·6, respectively) and intercepts were approximately 10 or less, except for PRO2 (21). The slopes of the COA streams are much larger than the reference sites (0·55 and 0·85 for PMRW and MTNC, respectively). The larger slopes of the COA streams compared with the reference streams indicate a carbonate-mineral weathering source. The reason for the larger ALK versus Si slopes for the Proctor Creek stations than COA stations is not evident from the geology or land use characteristics (Table II). For WOO1, the temporal variation of other parameters/constituents provides some additional information about sources as discussed below. In contrast to the large slopes at most of the COA stations, ALK was more poorly correlated with Si, at two headwater stations on the South River (SOU2 and SOU3) than those of other stations and although highly variable, the average ratio of ALK to Si was much lower. The likely cause of this result for these South River stations also is discussed in more detail at the end of this section

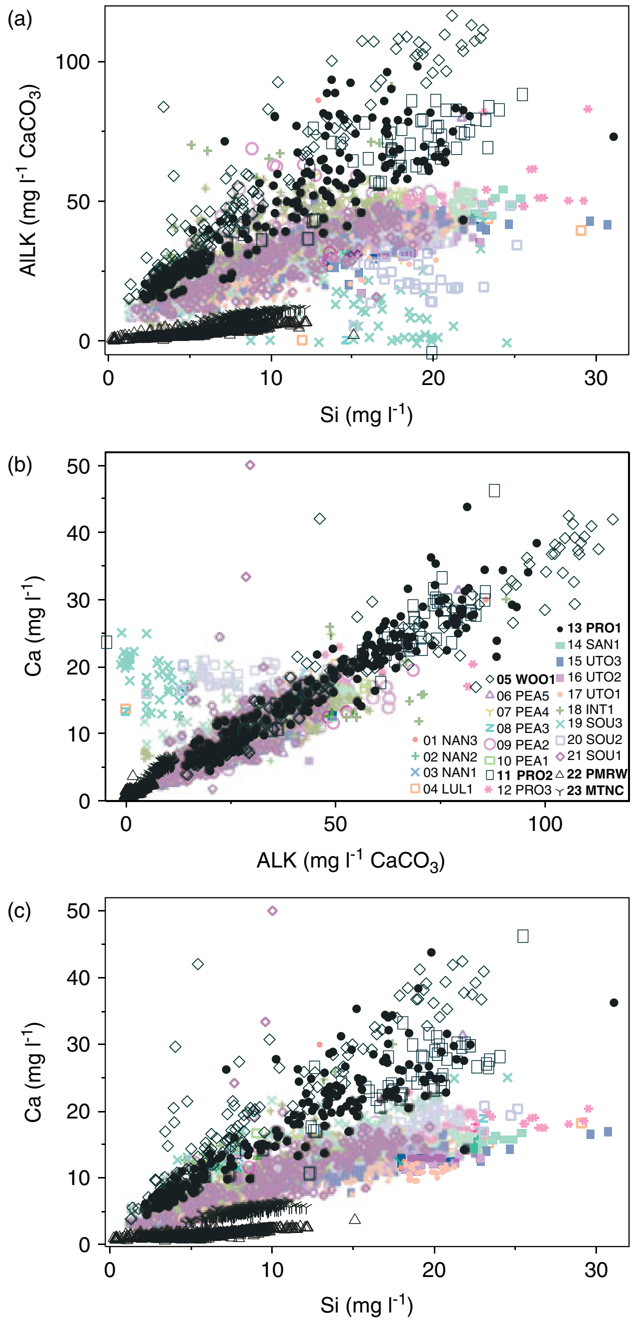

Figure 4. Concentration relations between (a) alkalinity and Si, (b) Ca and alkalinity and (c) Ca and Si of streams in the city of Atlanta and two reference streams, WY2004–WY2007

The bedrock composition is generally comparable across the study area and does not have any lithologic units dominated by carbonate minerals that could have a major affect the release rates of major ions (Higgins and Crawford, 2006). However, concrete is a major component of urbanized watersheds supporting the building and transportation infrastructure, and typically contains carbonate minerals (Matschel *et al.*, 2007). Furthermore, high Ca content of the concrete may dominate over the release of products generated from the natural or background mineral weathering of the soils and bedrock in watersheds. Assuming this to be the case, it is not surprising that Ca was highly correlated with ALK among most stations (Figure 4b), whereas the relation between Ca and Si should vary depending on the relative weathering contributions of basin materials and other potential sources (Figure 4c). Although Ca concentrations correlate with Si, linear regression slopes differ among stations. This result combined with the highly significant ($p < 0{\cdot}0001$) and similar linear relation between Ca and ALK among all COA stations also indicates a carbonate mineral source, which is most likely concrete.

Some other water quality differences are noted among COA monitoring stations, e.g. see pH in Figure 3a. Two stations had markedly different pH values compared with other stations; the pH of several samples at WOO1 were greater than 8·5 and at SOU3 were less than 6, which defines the range of the Georgia water quality standard (Georgia Environmental Protection Division [GA EPD], 2005).

The high pH of WOO1 was associated with high Ca, Mg and ALK concentrations, as discussed previously and suggests a carbonate source based on the these major ion relations. The WOO1 watershed (Woodall Creek) contains the highest percentage of commercial-plus-industrial land use (52·8%) and transportation, communications and utilities (14·1%) of any of the COA watersheds

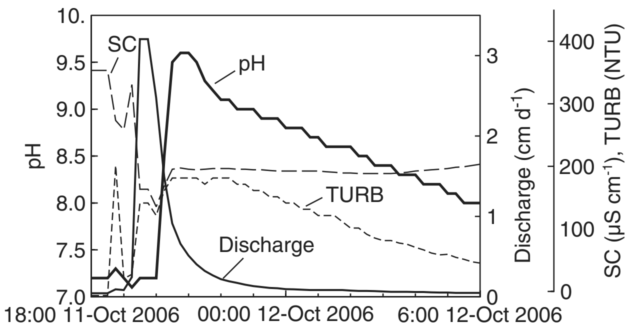

Figure 5. Real-time variations of pH, specific conductance, turbidity and discharge at WOO1 during a storm in October 2006

(Table II). An examination of the RT constituent variations of WOO1 reveals a consistent pattern of high-pH values (>9) during stormflow with pH increases occurring consistently after peak discharge, suggesting mobilization from a source distant from the gauging station (Figure 5). The high pH cannot be explained by the dissolution of carbonate minerals that would buffer the stream to a pH <9, and is more likely associated with leaching of a liquid Ca base or dissolution of Ca oxide (lye) or a Ca–Mg oxide, which might explain the high correlation among ALK, Ca and Mg concentrations (Stumm and Morgan, 1996). The higher percentage of commercial-plus-industrial, transportation, communications and utilities land use is indicative of more impervious surface than found in other watersheds (Table II). The COA Department of Watershed Management deployed a portable pH monitor on Woodall Creek in early 2007. The monitor has been systematically moved upstream and the results have narrowed the source to a headwater tributary, but their efforts have been hampered by the near absence of frequently recurring stormflow due to a long-term drought, which has affected the Atlanta Region since spring 2007.

High Cl concentrations occurred at LUL1, SOU1 and INT1 (Figure 3g). The high Cl concentrations at INT1 and LUL1 were associated with high Na concentrations (Figure 6a). INT1 is downstream from two combined sewer overflow (CSO) facilities including the following: (1) the Custer Street Regulator, a combined conveyance of stormwater to INT1 and treatment facility, which discharges treated stormwater to Intrenchment Creek before and after major storm runoff; and (2) a larger CSO facility downstream, which receives and treats CSO from the Custer Street Regulator and elsewhere during stormflow. The high Cl concentrations at INT1 were likely caused by chlorination of the CSO stormwater with sodium hypochlorite and subsequent conversion of the chlorine to chloride (O'Shea and Field, 1992). Most of the high Cl concentrations at INT1 also were associated with the low coliform bacteria concentrations (e.g. EC in Figure 6b), which is consistent with this hypothesis. The timing of outflow discharges from the National Pollutant Discharge Elimination System monthly Combined Sewer Overflow Monitoring Report for the Intrenchment Creek CSO was evaluated with respect to the USGS water quality monitoring data. High Na and Cl and low coliform bacteria concentrations in INT1 samples are associated with CSO discharges. In contrast, background stream-water quality, i.e. collected when the CSO was not discharging, was more enriched in Mg and other weathering products (see Mg relation with Cl in Figure 6c) and may be simply due to the relative enrichment of the CSO with by-products of the chlorination process, i.e. Na and Cl.

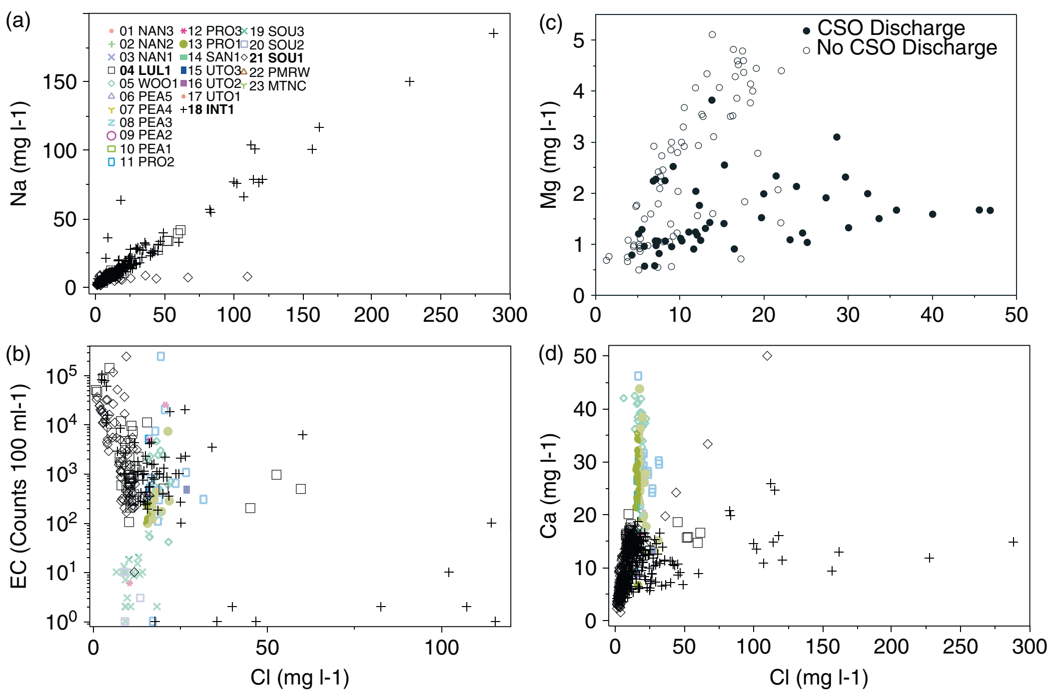

Figure 6. Concentration relations between (a) Na, (b) *E. Coli*, (c) Ca, (d) Mg and Cl of streams in the city of Atlanta and two reference streams for (a), (b) and (d) and INT1 for (c) during WY2004–WY2007

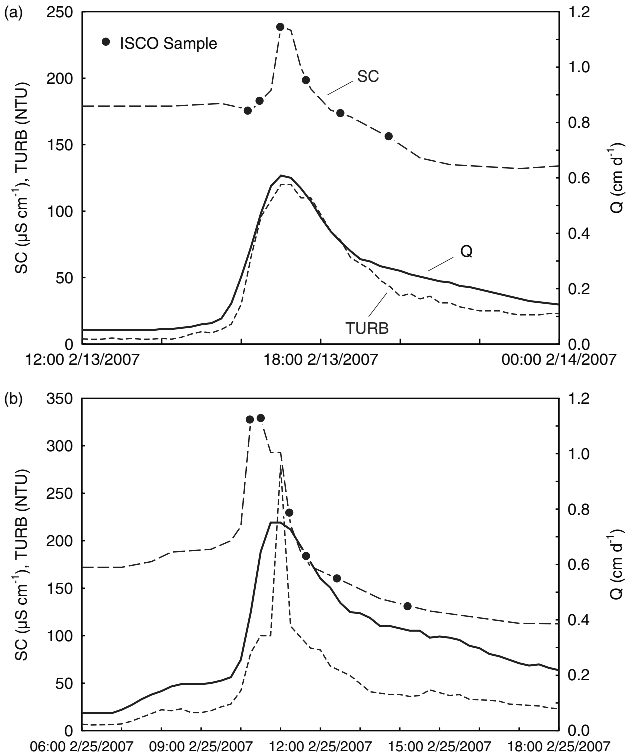

Figure 7. Real-time discharge, specific conductance and turbidity for SOU1, the South River at Forrest Park Road, for two rainstorms on (a) 13 February, 2007, and (b) 25 February, 2007

LUL1 is a small residential watershed, and a golf course covers a large percentage of the drainage area (Table II). The cause for the high Na and Cl concentrations is not as easily determined for LUL1 as it was for INT1. A possible cause was the periodic drainage of swimming pools, which also are chlorinated using sodium hypochlorite. The samples containing the high Na and Cl concentrations were collected during two different time periods, September 2003 and June 2004, which excludes the possibility that the cause was a single event.

The high Cl concentrations for samples collected at SOU1 occurred during two rainstorms in February 2007; the first rainstorm on 13 February followed a major winter storm that hit Atlanta on 1 February. Freezing conditions were anticipated for each rainstorm, but while major snowstorms affected the northeastern United States, only ~12 mm rainfall accompanied each rainstorm in the Atlanta Region. The high Cl concentrations at SOU1 were associated with high Ca concentrations (Figure 6d). The RT data showed a marked increase in SC during each event but with slight differences in the timing (Figure 7a and b for the rainstorms on 13 and 25 February, respectively). The high SC occurred at or slightly after peak streamflow during the 13 February rainstorm. During the 25 February rainstorm, the SC maximum was higher than that of the previous rainstorm and began to decrease prior to the peak streamflow. Decreases in SC below pre-event values occurred during the recession of each rainstorm. The likely source was dissolution of $CaCl_2$, which is a deicing salt. However, deicing salt usage records were not available from the COA Office of Transportation to confirm this hypothesis.

The water quality of SOU3 was highly degraded compared with the other COA streams and the reference streams. The pH and ALK were the lowest of all steams and SC, SO_4, NH_4N, NO_3N, Al, Mn, Cd and Zn concentrations were higher to much higher than other stations (Figure 3). In addition, it is likely that stream transport of these contaminants could explain the relatively high streamwater concentrations of some constituents at downstream stations. The pronounced chemical differences were attributed to transport of leachate, derived from the dissolution of residual alum waste, through contaminated groundwater contribution to the stream. An alum-manufacturing plant upstream from the COA boundary in East Point generates the waste, but it no longer uses surface impoundments for the alum, which likely had a direct impact on the stream (Tracy Hillick, COA, oral communication, 2006). Alum is an aluminum sulfate compound containing K, Na or NH_4N. The later form, ammonium alum [$NH_4Al(SO_4)_2$], is used in water treatment for coagulation, which causes settling of suspended particles and was the main product produced by the alum plant. Alum is relatively soluble and on dissolution, produces an acidic solution high in Al and SO_4, which would be partly neutralized by the ALK produced from weathering. The acid reaction with the ALK likely explains the non-characteristic relations between ALK and Si, and Ca and ALK (Figure 4a and b). The relatively higher NO_3N concentrations at SOU3 than at other stations would likely result from the oxidation of NH_4 released from the dissolution of ammonium alum, which is another acidifying reaction.

Nutrients. The nutrient species data for many samples were below the method-reporting limit. The number of samples affected by censoring has decreased with the improved detection/reporting limits as the study progressed. The distribution of nutrient concentrations for NH_4N, NO_2N, NO_3N, PO_4P and TP in Figure 3k–o is for samples with concentrations above the method-reporting limit and include 54, 68, 100, 30 and 63% of all of the samples analyzed, respectively. Nutrient concentrations, on average, were higher at the COA stations than at the reference stations. N species concentrations generally were much less than 10 mg l^{-1} NO_3N, the US Environmental Protection Agency (US EPA) drinking water standard (US EPA, 1986) and Georgia standard for wastewater disposal (GA EPD, 2005). Furthermore, less than 10% of the samples at each station exceeded 0·1 mg l^{-1} PO_4P, the US EPA recommended concentration limit for streams to prevent excessive algal growth (US EPA, 1986).

Bacteria and DO.

Some stations exceeded Georgia water quality standards (GA EPD, 2005). Samples collected at four stations (PEA2, PRO3, SOU1 and UTO1) were less than the minimum DO standard (4 mg l^{-1}), although the values were few, i.e. no more than three samples at any

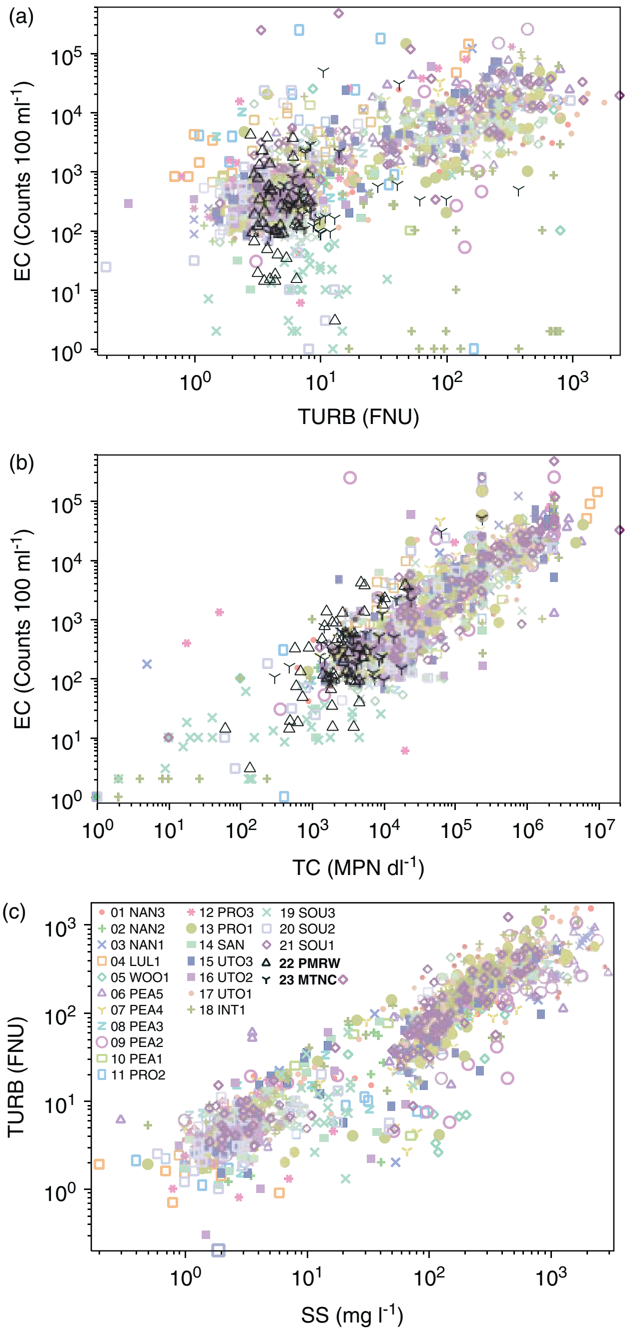

Figure 8. Relations between (a) *E. Coli* and turbidity, (b) *E. Coli* and total coliform and (c) turbidity and suspended sediment concentration of streams in the city of Atlanta, WY2004–WY2007, and two reference streams from April 2001 through March 2002

station (Figure 3s). In the worst case, only a few percentage of the 15-min data were less than 4 mg l^{-1} at the RT stations. The streams are generally well aerated and streamwater was more than 75% saturated with DO for more than 75% of the measurements at each station (Figure 3t).

In some cases, the skew of the concentration distribution was pronounced, e.g. coliform bacteria (EC, TC and FC), TURB and SS (Figure 3z–ad). The monitoring program was not designed to compute monthly geometric means for FC concentrations, the procedure for determining acceptability of stream water quality (GA EPD, 2005). Low bacteria concentrations (FC, TC and EC) were reported at INT1, which is affected by CSO chlorination, and SOU3, which is extremely acidic and has high trace metal concentrations, and for which no fish were detected during surveys conducted during 2001, 2003 or 2005 (Chrissy Thom, CH2M HILL, written communication, 2006). The degraded water quality conditions for SOU3 are similar to those of acidified streams due to acid mine drainage or acidic atmospheric deposition, where the low pH and high metal concentrations, particularly Al, are toxic to fish (Driscoll *et al.*, 2001). For the remainder of the stations, instantaneous FC concentrations of the 25th percentile of the sampling at the most rural stations, i.e. Sandy, Nancy and Utoy Creeks and 10th percentile at the other COA stations exceeded the Georgia water quality standard of 200 MPN dl^{-1} for any usage class. Furthermore, the FC concentrations of all high streamflow samples at these stations exceeded the Georgia water quality standard. In general, coliform bacteria concentrations were significantly correlated among each other (TC, FC and EC) and with TURB and SS (see Figure 8 for relations between (1) EC and TC, (2) EC and TURB and (3) TURB and SS). The TC, FC and EC concentrations at the COA stations were high, but were comparable to those reported for other urban streams (Makepeace *et al.*, 1995; Arienzo *et al.*, 2001; Ellis, 2004). These results also are consistent with results for the Chattahoochee River from the BacteriALERT Program, which was designed to provide a public alert when bacteria levels in the Chattahoochee River National Recreation Area exceed US EPA criteria (Lawrence, 2006). Although the concentrations are somewhat lower at the reference stations (from sampling conducted from April 2001 through March 2002), the relations among EC, TC and TURB are similar to those for the COA streams.

Metals. Trace metal concentrations were evaluated with respect to GA EPD standards (GA EPD, 2005). The chronic and acute criteria correspond to the US EPA definition for Criteria Continuous Concentration and Criteria Maximum Concentration, respectively; they are defined as the highest concentration of a pollutant to which aquatic life can be exposed for an extended period of time (4 days) and a short period of time (1-h average) without deleterious effects (US EPA, 2009). The chronic and acute values of Cd, Cu, Pb and Zn vary with hardness with the percentage of values exceeding the standard being determined by comparing sample values with the computed standard (GA EPD, 2005); the chronic and acute results are summarized for each sample type and station in Table III. The chronic and acute values shown for these metals on Figure 3 are for a hardness of 50 mg l^{-1} as $CaCO_3$. Few Cd concentrations exceeded the acute standard except at the South River stations, whereas noted previously the low pH likely enhanced metal mobility (Figure 3u and Table III). Concentrations of hexavalent Cr were below the acute and chronic standards for all but one sample at PEA4 (Figure 3v). The Cu and Zn concentrations of many samples at most

Table III. Percentage and number of samples for which concentrations of Cd, Cu, Pb and Zn exceed GA EPD standards, where the standard concentrations were computed from the sample hardness by equations developed by the US EPA and adopted by GA EPD (GA EPD, 2005)

Station	Type[a]	Cd								Cu								Pb								Zn							
		EWI		GRAB		ISCO		Total		EWI		GRAB		ISCO		Total		EWI		GRAB		ISCO		Total		EWI		GRAB		ISCO		Total	
		(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)
NAN3	A	0	(8)	NA	(0)	0	(83)	0	(91)	46·3	(41)	15·8	(19)	91·7	(108)	72	(168)	28·2	(39)	14·3	(14)	68·3	(123)	55·1	(176)	65·9	(41)	31·6	(19)	82·1	(123)	73·2	(183)
	B	0	(8)	NA	(0)	1·2	(83)	1·1	(91)	34·1	(41)	5·3	(19)	76·4	(123)	59·6	(183)	0	(39)	0	(14)	0	(123)	0	(176)	65·9	(41)	31·6	(19)	82·1	(123)	73·2	(183)
NAN2	A	0	(9)	0	(3)	NA	(0)	0	(12)	35·5	(31)	16·7	(18)	NA	(0)	28·6	(49)	24·2	(33)	15·4	(13)	NA	(0)	21·7	(46)	32·4	(37)	22·2	(18)	NA	(0)	29·1	(55)
	B	0	(9)	0	(3)	NA	(0)	0	(12)	27	(37)	16·7	(18)	NA	(0)	23·6	(55)	0	(33)	0	(13)	NA	(0)	0	(46)	32·4	(37)	22·2	(18)	NA	(0)	29·1	(55)
NAN1	A	0	(12)	0	(5)	1·3	(77)	1·1	(94)	35·9	(39)	25·0	(20)	95·9	(98)	72	(157)	17·6	(34)	26·7	(15)	67·3	(104)	52·3	(153)	23·1	(39)	25·0	(20)	82·7	(104)	61·3	(163)
	B	0	(12)	0	(5)	2·6	(77)	2·1	(94)	23·1	(39)	25·0	(20)	82·7	(104)	61·3	(163)	0	(34)	0	(15)	0	(104)	0	(153)	23·1	(39)	25·0	(20)	82·7	(104)	61·3	(163)
LUL1	A	0	(16)	0	(3)	NA	(0)	0	(19)	20·6	(34)	21·1	(19)	NA	(0)	20·8	(53)	12·1	(33)	11·8	(17)	NA	(0)	12·0	(50)	29·7	(37)	21·1	(19)	NA	(0)	26·8	(56)
	B	0	(16)	0	(3)	NA	(0)	0	(19)	13·5	(37)	15·8	(19)	NA	(0)	14·3	(56)	0	(33)	0	(17)	NA	(0)	0	(50)	29·7	(37)	21·1	(19)	NA	(0)	26·8	(56)
WOO1	A	0	(21)	0	(23)	0	(89)	0	(133)	50·0	(18)	60·9	(23)	86·5	(89)	76·9	(130)	19·0	(21)	47·8	(23)	59·6	(89)	51·1	(133)	90·0	(20)	91·3	(23)	95·5	(89)	93·9	(132)
	B	0	(21)	0	(23)	0	(89)	0	(133)	36·8	(19)	56·5	(23)	77·5	(89)	67·9	(131)	0	(21)	0	(23)	0	(89)	0	(133)	90·0	(20)	91·3	(23)	95·5	(89)	93·9	(132)
PEA5	A	0	(18)	0	(14)	2·9	(70)	2·0	(102)	36·4	(33)	45·5	(33)	93	(100)	72·3	(166)	22·2	(36)	45·2	(31)	70·6	(102)	55·6	(169)	47·2	(36)	63·6	(33)	95·1	(102)	78·9	(171)
	B	0	(18)	0	(14)	5·7	(70)	3·9	(102)	27·8	(36)	45·5	(33)	88·2	(102)	67·3	(171)	0	(36)	0	(31)	1	(102)	0·6	(169)	47·2	(36)	63·6	(33)	95·1	(102)	78·9	(171)
PEA4	A	0	(17)	0	(7)	3	(100)	2·4	(124)	34·2	(38)	25	(20)	85·8	(120)	68	(178)	22·9	(35)	0	(18)	62·5	(128)	48·6	(181)	56·4	(39)	38·1	(21)	90·6	(128)	77·7	(188)
	B	0	(17)	0	(7)	3	(100)	2·4	(124)	25·6	(39)	10	(20)	68·8	(128)	53·5	(187)	0	(35)	0	(18)	0	(128)	0	(181)	56·4	(39)	38·1	(21)	90·6	(128)	77·7	(188)
PEA3	A	6·7	(15)	NA	(0)	NA	(0)	6·7	(15)	47·7	(44)	0	(14)	NA	(0)	36·2	(58)	38·6	(44)	0	(13)	NA	(0)	29·8	(57)	47·7	(44)	7·1	(14)	NA	(0)	37·9	(58)
	B	6·7	(15)	NA	(0)	NA	(0)	6·7	(15)	40·9	(44)	0	(14)	NA	(0)	31	(58)	0	(44)	0	(13)	NA	(0)	0	(57)	47·7	(44)	7·1	(14)	NA	(0)	37·9	(58)
PEA2	A	0	(26)	0	(17)	1·1	(87)	0·8	(130)	40	(40)	40·9	(22)	98	(98)	75·6	(160)	26·2	(42)	27·3	(22)	82·7	(98)	60·5	(162)	56·1	(41)	59·1	(22)	95·9	(98)	80·7	(161)
	B	0	(26)	0	(17)	2·3	(87)	1·5	(130)	31·7	(41)	40·9	(22)	94·9	(98)	71·4	(161)	0	(42)	0	(22)	0	(98)	0	(162)	56·1	(41)	59·1	(22)	95·9	(98)	80·7	(161)
PEA1	A	0	(27)	0	(9)	NA	(0)	0	(36)	35·3	(34)	6·7	(15)	NA	(0)	26·5	(49)	18·4	(38)	6·7	(15)	NA	(0)	15·1	(53)	39·5	(38)	26·7	(15)	NA	(0)	35·8	(53)
	B	0	(27)	0	(9)	NA	(0)	0	(36)	28·9	(38)	6·7	(15)	NA	(0)	22·6	(53)	0	(38)	0	(15)	NA	(0)	0	(53)	42·1	(38)	26·7	(15)	NA	(0)	37·7	(53)
PRO2	A	0	(34)	0	(23)	NA	(0)	0	(57)	25	(32)	20·8	(24)	NA	(0)	23·2	(56)	20·6	(34)	41·7	(24)	NA	(0)	29·3	(58)	51·5	(33)	54·2	(24)	NA	(0)	52·6	(57)
	B	0	(34)	0	(23)	NA	(0)	0	(57)	18·2	(33)	16·7	(24)	NA	(0)	17·5	(57)	0	(34)	0	(24)	NA	(0)	0	(58)	51·5	(33)	54·2	(24)	NA	(0)	52·6	(57)
PRO3	A	0	(23)	0	(7)	NA	(0)	0	(30)	32·4	(34)	10·5	(19)	NA	(0)	24·5	(53)	17·1	(35)	5·6	(18)	NA	(0)	13·2	(53)	41·7	(36)	31·6	(19)	NA	(0)	38·2	(55)
	B	0	(23)	0	(7)	NA	(0)	0	(30)	22·9	(35)	5·3	(19)	NA	(0)	16·7	(54)	0	(35)	0	(18)	NA	(0)	0	(53)	41·7	(36)	31·6	(19)	NA	(0)	38·2	(55)
PRO1	A	0	(33)	0	(35)	1·9	(108)	1·1	(176)	32·4	(34)	54·3	(35)	87	(108)	70·1	(177)	20	(35)	37·1	(35)	75·9	(108)	57·3	(178)	38·9	(36)	62·9	(35)	88·9	(108)	73·7	(179)
	B	0	(33)	0	(35)	1·9	(108)	1·1	(176)	22·2	(36)	37·1	(35)	83·3	(108)	62·0	(179)	0	(35)	0	(35)	1·9	(108)	1·1	(178)	38·9	(36)	62·9	(35)	88·9	(108)	73·7	(179)
SAN1	A	0	(24)	0	(9)	NA	(0)	0	(33)	41·7	(36)	36·8	(19)	NA	(0)	40·0	(55)	17·1	(35)	29·4	(17)	NA	(0)	21·2	(52)	43·2	(37)	47·4	(19)	NA	(0)	44·6	(56)
	B	0	(24)	0	(9)	NA	(0)	0	(33)	21·6	(37)	21·1	(19)	NA	(0)	21·4	(56)	0	(35)	0	(17)	NA	(0)	0	(52)	43·2	(37)	47·4	(19)	NA	(0)	44·6	(56)
UTO3	A	0	(14)	0	(5)	5·3	(75)	4·3	(94)	35·9	(39)	20	(20)	90·4	(83)	65·5	(142)	32·4	(37)	17·6	(17)	83·1	(83)	61·3	(137)	43·6	(39)	25·0	(20)	86·7	(83)	66·2	(142)

DOI: 10.1002/hyp

Table III. (*Continued*)

Station	Type[a]	Cd								Cu							
		EWI		GRAB		ISCO		Total		EWI		GRAB		ISCO		Total	
		(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)
	B	0	(14)	0	(5)	12	(75)	9·6	(94)	27·5	(40)	10	(20)	84·3	(83)	58·0	(143)
UTO2	A	7·7	(13)	0	(11)	NA	(0)	4·2	(24)	25·0	(32)	33·3	(21)	NA	(0)	28·3	(53)
	B	7·7	(13)	0	(11)	NA	(0)	4·2	(24)	9·4	(32)	28·6	(21)	NA	(0)	17·0	(53)
UTO1	A	0	(24)	0	(16)	1·2	(81)	0·8	(121)	41	(39)	32	(25)	95	(101)	72·7	(165)
	B	0	(24)	0	(16)	2·5	(81)	1·7	(121)	35	(40)	24	(25)	89·1	(101)	66·3	(166)
INT1	A	2·9	(34)	6·5	(31)	1·7	(117)	2·7	(182)	41·7	(36)	48·5	(33)	89·9	(109)	72·5	(178)
	B	2·9	(34)	6·5	(31)	1·7	(117)	2·7	(182)	33·3	(36)	45·5	(33)	76·9	(117)	62·9	(186)
SOU3	A	55·0	(40)	82·4	(17)	14·3	(28)	47·1	(85)	95·0	(40)	94·1	(17)	100	(28)	96·5	(85)
	B	52·5	(40)	82·4	(17)	21·4	(28)	48·2	(85)	90·0	(40)	94·1	(17)	100	(28)	94·1	(85)
SOU2	A	10·3	(39)	23·5	(17)	NA	(0)	14·3	(56)	55·3	(38)	41·2	(17)	NA	(0)	50·9	(55)
	B	7·7	(39)	11·8	(17)	NA	(0)	8·9	(56)	39·5	(38)	35·3	(17)	NA	(0)	38·2	(55)
SOU1	A	0	(42)	0	(18)	0	(118)	0	(178)	39·5	(43)	5·6	(18)	92·6	(121)	71·4	(182)
	B	0	(42)	0	(18)	1·7	(118)	1·1	(178)	34·9	(43)	5·6	(18)	86	(121)	65·9	(182)

Station	Type[a]	Pb								Zn							
		EWI		GRAB		ISCO		Total		EWI		GRAB		ISCO		Total	
		(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)	(%)	(#)
	B	0	(37)	0	(17)	1·2	(83)	0·7	(137)	43·6	(39)	25·0	(20)	88	(83)	66·9	(142)
UTO2	A	11·5	(26)	13·3	(15)	NA	(0)	12·2	(41)	18·2	(33)	33·3	(21)	NA	(0)	24·1	(54)
	B	0	(26)	0	(15)	NA	(0)	0	(41)	18·2	(33)	33·3	(21)	NA	(0)	24·1	(54)
UTO1	A	37·1	(35)	21·7	(23)	74·3	(101)	58·5	(159)	97·4	(39)	100	(25)	100	(101)	99·4	(165)
	B	0	(35)	0	(23)	0	(101)	0	(159)	97·4	(39)	100	(25)	100	(101)	99·4	(165)
INT1	A	32·4	(37)	48·5	(33)	73·5	(117)	61	(187)	55·6	(36)	75·8	(33)	85·5	(117)	78	(186)
	B	0	(37)	0	(33)	1·7	(117)	1·1	(187)	55·6	(36)	75·8	(33)	85·5	(117)	78	(186)
SOU3	A	67·5	(40)	70·6	(17)	57·1	(28)	64·7	(85)	100	(40)	100	(17)	100	(28)	100	(85)
	B	0	(40)	0	(17)	0	(28)	0	(85)	100	(40)	100	(17)	100	(28)	100	(85)
SOU2	A	24·1	(29)	7·7	(13)	NA	(0)	19·0	(42)	100	(39)	100	(17)	NA	(0)	100	(56)
	B	0	(29)	0	(13)	NA	(0)	0	(42)	100	(39)	100	(17)	NA	(0)	100	(56)
SOU1	A	12·2	(41)	5·6	(18)	76·9	(121)	55·0	(180)	100	(42)	100	(18)	100	(121)	100	(181)
	B	0	(41)	0	(18)	3·3	(121)	2·2	(180)	100	(42)	100	(18)	100	(121)	100	(181)

Note: EWI, equal width increment; GRAB, manual point sample; ISCO, automated point sample.
[a] A = chronic, B = acute.

stations exceeded Georgia water quality chronic and acute standards and the Pb chronic standard (Table III and Figure 3u–y) These metals are ubiquitous in urban areas with sources ranging from highway runoff interacting with the washing off of metals derived from tire rubber particles to discarded and decayed metal fittings used in building construction (Sansalone and Buchberger, 1997; Gromaire-Mertz *et al.*, 1999; Davis *et al.*, 2001; Rose *et al.*, 2001; Sansalone *et al.*, 2005; Hudak and Banks, 2006).

Effect of streamflow on water quality

As noted above, some parameters and constituent concentrations differ markedly among stream sampling stations. However, some of the identified differences among stations may be an artifact of the type of sampling. The manual sampling was not fixed-interval sampling, which would have been primarily skewed towards base flow, but was designed to cover a range of hydrological conditions. Despite the attempt to provide a balanced hydrologic coverage, the manual sampling was more skewed towards base flow than stormflow (Figure 9a). In contrast, the ISCO samplers, which were only installed at the RT stations, targeted stormflows. Consequently, ISCO samples were skewed towards stormflows, particularly when compared with the manual sampling. The discharge at the time of sampling for the ISCO samples was significantly higher than for the GRAB samples ($p < 0{\cdot}005$) for each station except PEA2 and NAN1.

The relations between nutrient concentrations and flow generally were not statistically significant and varied among stations. However, TP and PO_4P concentrations were higher in the ISCO stormflow samples (Figure 9b and c) than the GRAB samples, but TP concentrations were not significantly correlated with PO_4P. Furthermore, TP concentrations correlated with TURB and SS concentrations, and these relations are attributed to the strong affinity for and related adsorption of P on Fe and Al oxides and hydroxides, a ubiquitous coating on soils in the southeastern United States. The TP concentrations were also highly correlated with Q as was TURB and SS, but the PO_4P concentrations did not correlate with Q. The cause of the generally higher PO_4P concentrations in the ISCO samples is not known, but it is not linked to higher discharge or sediment concentrations. In contrast, N species concentrations in GRAB samples were similar to ISCO samples, as shown for NO_3N in Figure 9d. As mentioned previously, flow was negatively correlated with the concentrations of weathering products as shown by the comparison of ISCO and GRAB sampling for Si (Figure 9e). Concentration distributions for EC, TURB and SS (Figure 3u–ad) show marked variability among stations, but most of the among-station differences are attributed to the difference in sampling method; SS, TURB and EC concentrations were much higher in the ISCO samples than in the GRAB samples (Figure 9f–h). The FC, EC and TC of most samples collected at SOU3 were very low until automatic sampling

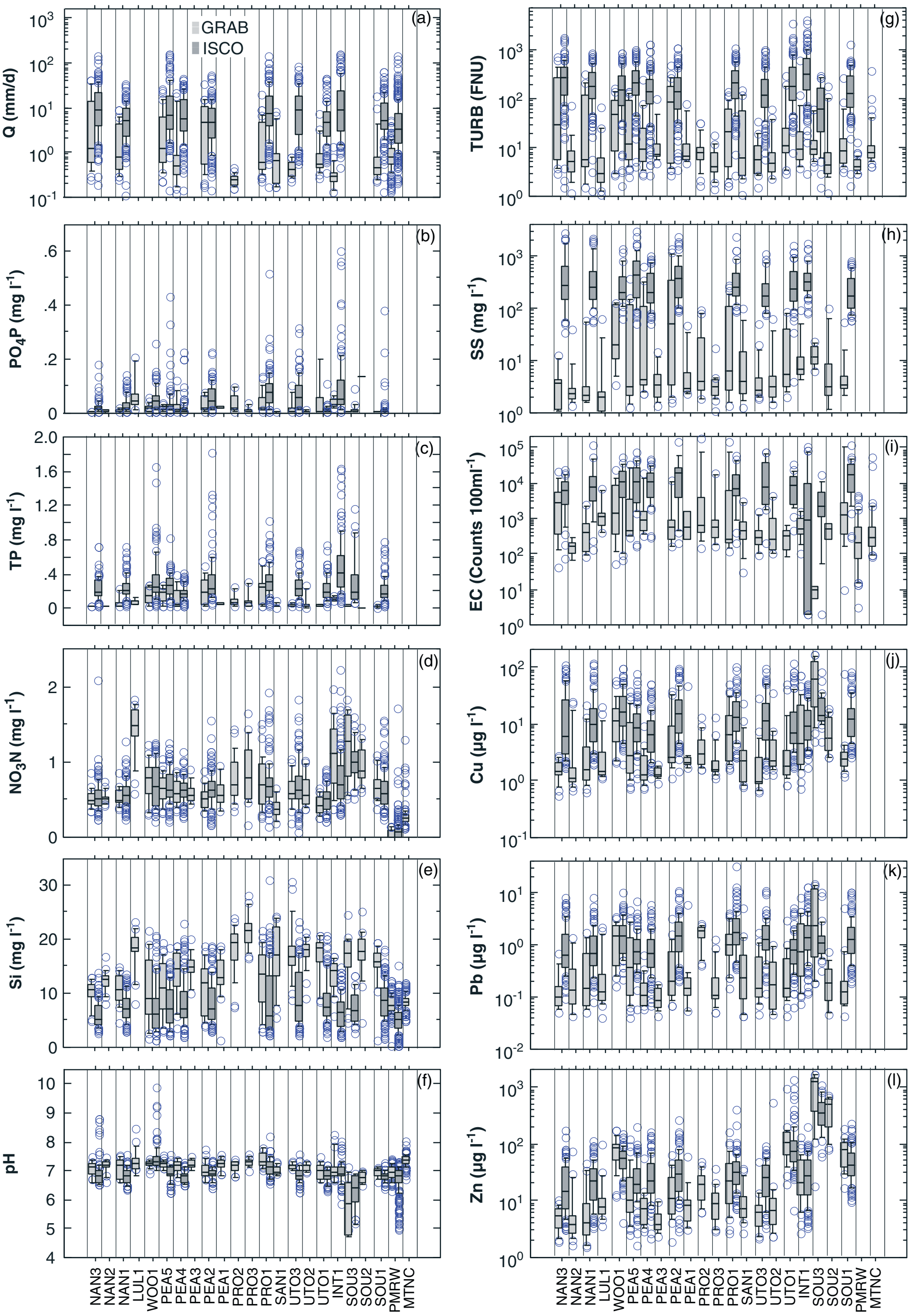

Figure 9. Distributions of (a) discharge (Q) and concentrations of (a) Q, (b) PO_4P, (c) TP, (d) NO_3N, (e) Si, (f) pH, (g) EC, (h) SS, (i) Cu, (j) Pb, and (k) Zn for GRAB and ISCO samples of streams in the city of Atlanta and two reference streams, WY2004–WY2007

began in 2007. The ISCO samples in 2007 had much higher and variable EC and TC. These samples were not analyzed for FC and box plot of bacteria concentrations (Figure 3z–ab) reflects this, i.e. the plots show low concentration for FC but much higher and variable concentrations for EC and TC.

The cause of the high concentrations of Cu, Pb and Zn can be qualified somewhat by the relations with sampling method. Cu, Pb and Zn are significantly higher in the ISCO samples than in the base flow dominated GRAB samples (e.g. Figure 9j–l). Also, a higher percentage of samples exceed Georgia water quality standards for these metals in the higher flow ISCO samples than in the lower flow GRAB or EWI samples (Table III). These metals likely originate in runoff during rainstorms, possibly from washoff of the metal that accumulates on impervious surfaces (Revitt and Ellis, 1980; Ellis *et al.*, 1986; Davis *et al.*, 2001;

Rose *et al.*, 2001; Sansalone *et al.*, 2005). However, Cu, Pb and Zn concentrations although highly correlated with each other, generally are not correlated with discharge or TURB. Furthermore, the metal concentrations of the ISCO samples show hysteresis with the highest concentrations generally occurring during the beginning of stormflow, but not for every storm. The storms with high concentrations at the beginning of the storm are consistent with a first-flush phenomenon as observed in urban streams elsewhere (Sansalone and Buchberger, 1997; Lee *et al.*, 2005). However, the concentrations discharge relations vary with the storms and it is likely that the variation is caused by the routing and mixing of runoff, which would be partly dependent on the spatial and temporal rainfall characteristics. Also, the concentrations vary by site and storm, which is consistent with results of a first-flush assessment of some Texas streams that displayed a more consistent pattern of first flush of metals than at the COA streams (Appel and Hudak, 2001).

For the few ISCO storm samples collected at SOU3 during 2007 after the RT station was installed, metal concentrations were lower in the ISCO compared with the GRAB samples. The pH values are also higher in the ISCO samples than GRAB samples at SOU3 indicating that the acidification due to dissolution of alum occurs during base flow, when groundwater contributions are the highest. These results suggest that groundwater near the alum-manufacturing plant is highly acidic and contains high metal concentrations, a result that has not been confirmed.

CONCLUSIONS

A long-term stream water quality monitoring network was established in the COA during 2003 to assess baseline conditions and the effects of several management operations on stream water quality. Routine hydrologically based stream sampling was conducted at 21 stations, with drainage areas ranging from 3·7 to 232 km^2; 11 of the stations are RT water quality stations having continuous measures of stream stage (which is converted to discharge), pH, DO, SC, water temperature and TURB, and automatic samplers for stormwater collection. The samples are analyzed for field parameters and a broad suite of dissolved and sediment-related constituents. The objectives of this study are the following: (1) to evaluate water quality differences among COA streamwater sampling stations with respect to field parameters and concentrations of the dissolved major ions, minor and trace metals, nutrients and bacteria; (2) to compare COA stream water quality for a subset of parameters to those at nearby reference stations including a small (0·4 km^2) relatively undisturbed forested watershed and a larger (10 km^2) low-density residential watershed; and (3) to evaluate the water quality differences among and within COA sampling stations with respect to differences in land-use characteristics and other environmental factors including streamflow.

Urbanization affects water quality. The drainage areas of the 21 COA stations are highly urbanized with 69 to 96% urban land use. Concentrations of most constituents were significantly higher at COA stations than at two nearby reference stations. Sufficient information about variations in urban stream water quality derived from routine manual sampling, automatic sampling during stormflows and RT water quality monitoring provided plausible hypotheses for observed differences in water quality among streams in the COA.

For the COA stations, ALK, ALK to Si concentration ratios and Ca and Mg concentrations were much higher than for the reference stations. These differences are consistent with a carbonate mineral weathering source of the Ca, Mg and ALK in COA streams, which is hypothesized to be concrete. For WOO1, the slope of a linear regression of ALK on Si is much higher than the other COA streams indicating another possible source. Also, RT pH was very high (>9) during stormflows exceeding the pH associated with carbonate dissolution, and the pH maximum consistently lagged peak streamflow. The WOO1 results indicate the possible dissolution and mobilization of a Ca or Ca–Mg base or oxide such as lye from a point source in the headwaters.

High Cl concentrations occur at three stations and are hypothesized to be associated with discharges of chlorinated CSO to Intrenchment Creek (INT1), draining of swimming pool(s) in the Lullwater Creek basin (LUL1) and dissolution and transport during rainstorms of $CaCl_2$, a deicing salt, on the South River (SOU1), which also was indicated by RT data. The headwater station on the South River (SOU3) is a highly degraded stream affected by the dissolution and transport of ammonium alum [$NH_4Al(SO_4)_2$] from an alum plant upstream outside the COA boundary in East Point. SOU3 has low pH (<5), low ALK and high concentrations of SO_4, NH_4N, NO_3N, Al, Mn, Cd and Zn, and no fish were found in the stream during any survey conducted since 2000. The effects of the alum on water quality were diminished, but observable at the two downstream stations, SOU2 and SOU1.

More than 90% of the FC concentrations exceeded the US EPA standard of 200 MPN dl^{-1} for any water usage class. Coliform bacteria concentrations (FC, TC, EC) were highly correlated among type and with TURB and SS concentrations. Nutrient concentrations generally were high compared with the nearby reference stations, but were low compared with US EPA standards. Many samples were below the analytical-method reporting limit for PO_4P, TP and NH_4N. The streams are well aerated and only a few samples showed low DO concentrations.

Concentrations of most of the major ions decreased with increasing streamflow as observed, but increased with increasing streamflow for several SS-related constituents such as TP, PO_4P, TURB, SS and coliform bacteria, particularly at RT stations. These relations also were observed in a comparison of the manual GRAB samples and automated samples. The distribution of streamflows for the GRAB samples was skewed towards base flow, despite attempts to collect samples over a range of streamflows; rainstorms typically occur at night and are hard to predict. In contrast, the automated samples targeted stormflows. Some trace metals (Cu and Pb) were higher in automated storm samples than in the manual samples indicating mobilization during rainstorms, but concentration–discharge relations varied among storms.

ACKNOWLEDGEMENTS

This study is a contribution of the city of Atlanta Long-Term Water Quality Monitoring Program and was conducted in cooperation with the city of Atlanta. I am grateful to the technical oversight provided by a technical advisory committee, which is chaired by Upper Chattahoochee Riverkeeper and has representatives from public agencies including Cobb County—Marietta Water Authority, Gwinnett County Department of Public Utilities, Georgia Environmental Protection Division and US Environmental Protection Agency and universities including Georgia Institute of Technology, the University of Georgia and Georgia State University. Any use of trade, firm or product names is for descriptive purposes only and does not imply endorsement by the US government.

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