Report for 2005GA74B: A strontium isotope investigation of possible sewage influx to stream base flow in the Atlanta metropolitan region

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Report Follows

A Strontium Isotopic Investigation of Possible Sewage Influx to Stream Base Flow in the Atlanta Metropolitan Region

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EXECUTIVE SUMMARY

Major Findings of the Study: Strontium isotope ratios did *not* provide a meaningful indicator of sewage effluent pollution in the urbanized Atlanta portion of the Chattahoochee River Basin. Any degree of urbanization within the Chattahoochee Basin results in base flow solute concentrations that are significantly elevated above "background". The basin-wide correlation between sodium, potassium, and chloride indicates pervasive low-level contamination from human waste effluent.

Abstract: The hydrochemistry (major ions concentrations, stable oxygen isotope ratios, tritium concentrations, strontium ion concentrations, strontium isotope ratios and hydrology) of base flow within the upper 6,940 km^2 of the Chattahoochee River Basin (CRB) in Georgia was investigated on a synoptic basis during a dry period in May, 2005. The primary objective of the study was to determine whether strontium ion concentrations and strontium isotope ratios when analyzed in conjunction with major ion trends could provide a "signature" of sewage effluent contamination within stream base flow. The 39 samples acquired for this study were representative of rural basins, semi-developed basins, the Chattahoochee River, urbanized basins within the Atlanta Metropolitan Region (AMR), sewered basins within the AMR, combined sewage overflow (CSO) basins, and sewage effluent.

Strontium ion concentrations were highly elevated (>75 μg/L) in those streams in which base flow solute concentrations were also elevated (TDS >100 mg/L), probably as the result of sewage effluent imposition. Although there is a very wide range of strontium isotope ratio variation ($0.709460 < {}^{87}Sr/{}^{86}Sr < 0.723274$), there is no unique "waste signature' in that the range of natural variation within the rural basins that are not impacted by waste disposal encompasses virtually the total range of isotope ratios for the study area. There is also a wide range of geochemical variation and the general trend in terms of *increasing* solute concentrations is: rural basins < Chattahoochee River < semi-developed basins < AMR basins without a main sewer line < AMR basins with a main sewer line < CSO basins < sewage effluent. Major ion concentrations within base flow of the Chattahoochee River significantly increase within the AMR and remain above upstream levels far downstream of the AMR. The most likely source of the increased source of solutes within the impacted basins is contamination within the near-stream zone.

The highest degree of correlation ($r^2 > 0.80$) for the major ions in base flow was between chloride, sodium, and potassium which are all concentrated within sewage effluent and are dominant ions present in human electrolytes and household cleaning fluids. These correlations would *not* be expected if aluminosilicate weathering was the sole control upon the major ion geochemistry of base flow (which is ground water). The relatively high sulfate concentrations (mean SO_4 = 27.8 mg/L) for the group of basins which include a main sewage line parallel and proximal to a stream suggests that some ground water pollution originates from leaky buried conveyance pipes in that sulfate is concentrated within sewage effluent. However, the major ion chemistry as a whole is equivocal in this regard in that all urban and semi-urban basins other than the rural basins are characterized by relatively high chloride, alkalinity, Sr ion, and TDS concentrations. Any degree of urbanization or development results in solute concentrations that are significantly greater than "background". The sources of these solutes are not always clear and are likely diffused throughout the developed and developing Atlanta Metropolitan Region.

KEY WORDS: Chattahoochee River Basin, Atlanta Metropolitan Region, base flow, major ion geochemistry, Piedmont Province hydrochemistry, strontium ion concentrations, strontium isotope ratios, urban hydrology

PROJECT DESCRIPTION

Introduction: Overview of Water Quality Problems in the Atlanta Metropolitan Region:

The Chattahoochee River is the most utilized water resource in Georgia (Frick and Gregory, 2000) and provides the principal water resource for more than 4.5 million people who currently live within the Atlanta Metropolitan Region (AMR). The Chattahoochee River Basin (CRB) is virtually totally urbanized from Roswell, GA (~20 miles north of the City of Atlanta) to approximately 20 miles south of the city. The AMR occupies a 12-county, 1,200 square mile region and hence has a potentially large impact upon water quality within the Chattahoochee River well downstream of Atlanta.

The most important water quality problem faced by residents of the CRB and its water managers is the imposition of sewage wastes to the Chattahoochee River and its tributaries. On average ~6.0×10^5 cubic meters of sewage is conveyed daily to treatment facilities in the City of Atlanta (Seabrook, 1997) and is eventually discharged to the Chattahoochee River. The City of Atlanta is underlain by 3,400 km (2,100 miles)of sewage discharge pipe and the average age of these pipes is 75 years (Q. Aslami, City of Atlanta Bureau of Sewer Operations, 2001, personal communication). This is an antiquated system that periodically backs up and overflows through manhole covers. These pipes likely discharge polluted effluent into the subsurface at various locations; however, the extent of this problem is not well known. In some cases contaminants are directly flushed through this system as storm flow; while in other cases a given pollutant might accumulate within the riparian zone, pollute the ground water below a stream and subsequently contaminate base flow (i.e. stream flow that occurs between storms). The controls upon base flow contamination have been far less studied and are less understood than those related to surface water pollution. This is true with respect to the Chattahoochee River Basin (CRB), urban basins, and watersheds in general.

The major problem associated with sewage wastes from leaky pipes as well as from untreated sewage effluent is coliform bacteria contamination which is the most common reason that the Chattahoochee River and its tributaries at times do not meet designated standards for drinking water supply (Gregory and Frick, 2000). In various small urban basins within the AMR such as Proctor Creek and Clear Creek the problem is exacerbated by combined sewage overflow (CSO) facilities that discharge sewage effluent into these tributaries of the Chattahoochee River. During periods following intense storms, sewage is frequently discharged to stream basins through overflowing manhole covers. Gregory and Frick (2000) observed an inverse relationship between bacteria concentrations and discharge in several highly urbanized watersheds. These authors inferred a possible ground water source for these contaminants and the origin of this contamination was from CSOs or leaky sewage pipes. Another possible source of bacterial contamination within the urban environment include wastes generated by domestic pets (Center for Watershed Protection, 1999).

In addition to the sewage problem, rapid growth (*urban sprawl*) into the northern suburbs such as Forsyth and Cherokee County is placing additional stress upon the limited water and land resources of the Upper Chattahoochee Basin. The NAWQA Program of the U.S. Geological Survey

has documented that the AMR is a major source area responsible for elevated pesticide, fertilizer, polycyclic aromatic hydrocarbons (PAHs), metal and suspended sediment concentrations within the Apalachicola - Chattahoochee - Flint River Basin. Most of the load of these contaminants can not be attributed to specific source areas and is associated with storm runoff rather than base flow (Frick et al., 1998).

Major ion concentrations within the urban tributaries of the Chattahoochee River Basin (CRB) are often greater than less urbanized Piedmont basins; however, are typically below Maximum Concentration Limits (MCLs) for drinking water (Rose, 2002). Therefore the major ion geochemistry of these basins has been given relatively little attention in comparison to the study of bacteria, pesticides, metals and other contaminants associated with storm runoff (i.e. Frick et al., 1998). Nonetheless, total dissolved solid (TDS) solid concentrations within the Chattahoochee River downstream of the Atlanta region have been elevated for many decades (McConnell and Buell, 1994). The source(s) and source area(s) for these wastes remains poorly understood but in some cases is related to sewage effluent problems (Rose, 2002).

Objectives of the Research Project:

Given the ongoing concern with sewage contamination in the CRB, the objective of the research summarized in this report was to analyze possible new "tracers" for sewage effluent in stream base flow. Specifically, strontium isotope ratios ($^{87}Sr/^{86}Sr$) and strontium ion concentrations were analyzed in conjunction with *environmental* isotopic data (tritium concentrations and stable oxygen isotope ratios) and the major ion geochemistry of base flow in streams and waste water facilities within the 2,680 square mile (6,940 km^2)area of the Chattahoochee River Basin upstream of Franklin, Georgia in Heard County. A related objective of this investigation was to derive and interpret a large *synoptic* (i.e. that representative of the same sampling period) hydrogeochemical and isotopic data set that can be used to better interpret the sources and extent of base flow contamination within the CRB. This multiple-parameter approach allowed for the comparative analysis of the effects of land use and waste disposal activity in this very large study basin.

BACKGROUND: UTILIZATION OF STRONTIUM ISOTOPE RATIOS IN STREAM BASIN STUDIES

Some prefatory explanation regarding the utilization of strontium isotopes is necessary in that this is not a universally utilized "tracer" in watershed hydrology. Strontium isotope ratios have been utilized in previous watershed studies primarily to trace water pathways and define weathering reactions that control the major ion chemistry of stream flow (Bullen and Kendall, 1998). Strontium isotope ratios have also been used for many other purposes including the analysis of: 1) mixing dynamics between saline and fresh water in sedimentary basins (Banner et al., 1989 and Musgrove and Banner, 1993); 2) fluvial contributions of strontium to sea water (Goldstein and Jacobsen, 1987; Waldeigh et al., 1985; and Palmer and Edmond, 1992); 3) source rock contributions to the solute load of river water (Miller et al., 1993, Krishnaswami et al., 1992; and Aubert et al., 2002); 4) ground water - surface water interactions (Katz et al., 1997) and leakage processes in aquifers

(Woods et al., 2000); 5) the paleohydrology of the proposed Yucca Mountain tuff nuclear waste repository (Stuckless et al., 1991 and Johnson and DePaolo, 1994); 6) tracing of hydrologic flow paths in watersheds (Hogan and Blum, 1993) and 7) the sources of waters to lakes, playas, and peat bogs (Neumann and Dreiss, 1995; Lyons et al., 1995 and Hogan et al., 2000).

The first-order control upon the $^{87}Sr/^{86}Sr$ ratio in natural waters is the relative abundance of aluminosilicate minerals versus carbonate minerals comprising either a watershed or aquifer (Bishop et al., 1994; Douglas et al., 2002 and Krishnaswami et al., 1992). Strontium isotopes do not significantly fractionate as a result of biological or low-temperature abiotic chemical reactions and hence their ratio will be a function primarily of weathering reactions (Hunt et al., 1998). In general, waters that derive their strontium from carbonate minerals will be characterized by lower $^{87}Sr/^{86}Sr$ ratios and higher Sr concentrations than those waters in which strontium evolves from the Rb-rich aluminosilicates (McNutt et al., 1990; Bullen and Kendall, 1998; and Palmer and Edmond, 1992). Biotite is the most of the common source of Sr-87 that is derived from the beta decay of rubidium-87 and rubidium is a common substitute for potassium in this mineral(Bullen and Kendall, 1998). Other potential sources of Sr-87 within aluminosilicate watersheds include K-feldspar, garnet and hornblende (Bailey et al., 1996). Strontium isotopic ratios of natural waters typically better reflect the ratios of individual minerals rather than whole rock ratios because of the variability inherent in weathering rates for minerals (Aubert et al., 2002).

There are numerous controls upon $^{87}Sr/^{86}Sr$ ratios in addition to source minerals that when properly interpreted can lead to a better understanding of the hydrodynamics of watersheds and aquifers. The $^{87}Sr/^{86}Sr$ ratio of rainwater is usually much different from that of a solution derived from mineral weathering and therefore the isotopic composition might indicate the relative contribution of recent precipitation to a natural water source (Bailey, 1996; Hogan et al., 2000 and Douglas et al., 2002). There is often a strong correlation between the rate of discharge or water flux and strontium isotope composition. Aubert et al. (2002) found that strontium isotope ratios correlated positively with discharge rates in the Strengbach catchment of the Vosges mountains of France and attributed this relationship to a variable source area effect (i.e. the relative contribution from hillslopes). Variable discharge rates are often controlled by soil water-ground water mixing processes and other factors that also control the isotopic composition of strontium (Land et al., 2000 and Négrel and Lachassagne, 2000). The age of minerals is another control upon the $^{87}Sr/^{86}Sr$ ratio in that the isotopic composition of strontium within minerals has changed with time and the susceptibility to weathering of various minerals is also a function of time (Goldstein and Jacobsen, 1987 and Blum et al., 1994).

Cation exchange reactions represent still another control upon the isotopic composition of stream water. Miller et al. (1993) concluded that cation exchange reactions contributed to an average of 30% of the strontium exported in stream water in a high elevation watershed in New York and showed that there is a $^{87}Sr/^{86}Sr$ gradient in soil columns within this study area. In addition to providing a variable isotopic pool of strontium in the upper soil horizons, such gradients may result in variable strontium isotope ratios in stream water. Finally, pollutant influxes from sewage, mining tailings, waste dumping, and fertilizer may affect the magnitude and variability of the $^{87}Sr/^{86}Sr$ ratio in stream water (Tricca et al., 1999 and Soler et al., 2002). However, the utilization of strontium

Sample No.	Stable Oxygen Ratio $\delta^{18}O$ per mil ($^o/_{oo}$) relative to SMOW[a]	Stable Oxygen Ratio $\delta^{18}O$ per mil ($^o/_{oo}$) relative to SMOW (repeat analysis)	Tritium (^3H) Concentration (in T.U.)[b]
CB-23	-5.45		
CB-24	-5.42	-5.43	
CB-25	-5.23		
CB-26	-4.24		
CB-27	-4.96		
CB-28	-4.54		
CB-29	-4.40		
CB-30	-4.34		
CB-31	-4.28		
CB-32	-4.34		8.3±0.8
CB-33	-4.42	-4.38	
CB-34	-4.17		
CB-35	-3.72		
CB-36	-4.64		8.0±0.7
WTP-1	-4.53	-4.40	
WTP-2	-4.44		
Average Stream Water Composition = -4.64 $^o/_{oo}$ ± 0.48 $^o/_{oo}$ (1 std. dev.) [a]) SMOW = Standard Mean Ocean Water [b]) T.U. = Tritium Unit (1 tritium atom in 10^{18} H atoms)			

Major Ion Geochemistry:

General Trends and Comparison of Sub-Groups: The major ion chemistry of stream base flow in the Chattahoochee Basin (as summarized in Table 4 and Appendix 2) is extraordinarily diverse and this diversity can not be solely attributed to lithological variation. There is assumably a reasonably varied assemblage of minerals and rocks within the rural basins that were sampled both north and south of the AMR; however, there was only a fairly narrow range of hydrochemical variation (i.e. TDS < 50 mg/L) within these basins. Therefore the effects of anthropogenic contamination must be considered. The term '*contamination*' as used in this study refers to solute that is input as a result of some human activity that results in ionic concentrations that are significantly greater than "*background*" or *lithogenic* concentrations. The term "*contamination*" does not necessarily imply that the concentration of a given parameter is elevated above Maximum Concentration Levels (MCLs) for drinking water and in fact major ion concentrations for all the stream water is below the MCLs for drinking water (i.e. <250 mg/L chloride, <250 mg/L sulfate, and < 500 mg/L for total dissolved solids [TDS]).

The relatively large amount of diversity observed within this synoptic sample set is summarized in the *Stiff diagrams* shown in Figure 4. The variable shapes of each polygon in this figure represent different proportions of the major ions (Ca, Na, K, Mg, HCO_3, Cl, and SO_4) while the area of the polygon corresponds to the total ionic load or TDS of the individual sample. The most obvious observation that can be inferred from Figure 4 is that the stream chemistry of all the other groups (as represented by these particular individual streams) is far more concentrated in solute than the rural streams (represented by Acorn Creek which is a small watershed south of the AMR). Furthermore, it can be inferred from Figure 4 that Chattahoochee River water more closely resembles the geochemistry of rural basin water (considered to represent "background" or uncontaminated conditions) than it does waters from the urban areas. We can also infer from Figure 4 that stream flow in the semi-developed basins (represented by Olley Creek - west of Atlanta) much more closely resembles the major ion geochemistry of stream water in the developed basins (i.e. South Peachtree Creek) than base flow in the rural basins. Further details on these observations will be forthcoming.

The highest TDS concentrations in stream water were 236 mg/L for Proctor Creek which is directly downstream from a CSO facility and the lowest value was 16 mg/L for Smith Creek which is a head water stream in the Chattahoochee National Forest in the Blue Ridge Mountains (Table 4). For purposes of comparison, TDS concentrations in sewage effluent were between 250 and 350 mg/L in the two samples that were obtained from R.N. Clayton and Utoy Creek water treatment plants. The variability with respect to specific conductance (a readily measurable proxy for total solute concentrations or TDS) is shown on Figure 5. The patterns of groupings observed on Figure 5 are common to most all of the major ions in that it shows that urban sub-groups (i.e. semi-developed basins, developed basins, basins with main sewage line basins, and basins with CSOs) are characterized by higher solute concentrations than both rural base flow and Chattahoochee River base flow.

Bicarbonate (as determined by alkalinity titration)was the most concentrated of the ions which is typically the case in aluminosilicate watersheds such as the Chattahoochee River basin and other watersheds within the Blue Ridge and Piedmont Provinces. Bicarbonate concentrations were

Table 4
Summary of Chemical Data by Groups

Specific Conductance (values in μS/cm)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	33.2	34.1	17.9	10.2	56.1
II	Chattahoochee River	9	77.4	74.6	34.6	37.1	136.3
III	Semi-Developed Basins	7	95.2	105.9	41.3	70.5	167.9
IV	Developed Basins in the AMR[1]	5	109.5	116.2	20.5	91.0	143.9
V	AMR Basins with Streams on Main Sewage Line	5	131.1	136.3	16.7	121.9	160.1
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	224.3	245.8	53.3	206.5	306.5
VII	Sewage Effluent	2	------	430.1	42.3	400.2	460.2
pH							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	6.1	6.1	0.1	5.9	6.3
II	Chattahoochee River	9	6.3	6.3	0.3	5.8	6.7
III	Semi-Developed Basins	7	6.4	6.4	0.2	6.1	6.7
IV	Developed Basins in the AMR[1]	5	6.5	6.4	0.1	6.4	6.6
V	AMR Basins with Streams on Main Sewage Line	5	6.5	6.5	0.1	6.4	6.8
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	6.7	6.7	0.4	6.2	7.1
VII	Sewage Effluent	2	------	6.7	0.2	6.5	6.8

[1]AMR= Atlanta Metropolitan Region

Table 4
Summary of Chemical Data by Groups (continued)

Bicarbonate Alkalinity (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	9.2	12.2	7.0	3.9	22.7
II	Chattahoochee River	9	22.4	20.2	6.9	10.7	31.5
III	Semi-Developed Basins	7	32.5	32.7	2.5	27.7	35.0
IV	Developed Basins in the AMR	5	41.7	42.0	6.8	34.3	52.5
V	AMR Basins with Streams on Main Sewage Line	5	43.1	44.5	8.0	35.4	56.9
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	67.1	68.6	21.0	48.3	90.3
VII	Sewage Effluent	2	------	110.4	64.6	64.7	156.1
Chloride (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	5.4	5.4	2.2	1.7	8.2
II	Chattahoochee River	9	11.4	11.5	5.9	4.5	21.9
III	Semi-Developed Basins	7	12.1	17.0	15.4	4.7	49.3
IV	Developed Basins in the AMR	5	13.2	14.7	5.2	8.5	22.0
V	AMR Basins with Streams on Main Sewage Line	5	14.5	14.9	2.5	12.0	18.2
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	28.9	31.7	6.6	27.1	39.2
VII	Sewage Effluent	2	-----	66.2	1.5	65.1	67.3

Table 4
Summary of Chemical Data by Groups (continued)

Sulfate (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	1.9	1.9	0.4	1.1	2.7
II	Chattahoochee River	9	5.6	5.6	2.8	1.8	10.4
III	Semi-Developed Basins	7	4.1	6.6	6.0	2.2	19.0
IV	Developed Basins in the AMR	5	4.9	5.3	1.4	3.7	7.6
V	AMR Basins with Streams on Main Sewage Line	5	11.9	14.2	5.0	11.1	23.1
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	27.9	27.8	14.0	13.8	41.8
VII	Sewage Effluent	2	------	27.3	2.7	25.4	29.2
Calcium (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	1.2	2.3	2.2	1.3	6.3
II	Chattahoochee River	9	3.2	4.3	2.5	1.4	9.1
III	Semi-Developed Basins	7	6.9	6.7	1.9	6.9	10.1
IV	Developed Basins in the AMR	5	10.4	10.4	3.4	5.9	13.8
V	AMR Basins with Streams on Main Sewage Line	5	10.9	12.0	3.2	9.4	17.5
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	25.4	25.0	5.7	19.1	30.5
VII	Sewage Effluent	3	-----	20.3	8.6	14.2	26.4

Table 4
Summary of Chemical Data by Groups (continued)

Magnesium (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	0.7	0.7	0.4	0.2	1.4
II	Chattahoochee River	9	1.2	1.1	0.3	0.7	1.6
III	Semi-Developed Basins	7	2.0	2.4	1.2	1.8	5.1
IV	Developed Basins in the AMR	5	1.9	2.0	0.1	1.9	2.1
V	AMR Basins with Streams on Main Sewage Line	5	2.4	2.5	0.3	2.2	3.1
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	3.8	3.7	1.4	2.3	5.1
VII	Sewage Effluent	2	-----	2.6	0.2	2.4	2.8
Sodium (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	4.1	3.8	1.8	1.3	6.3
II	Chattahoochee River	9	7.5	8.4	5.2	3.1	19.5
III	Semi-Developed Basins	7	6.1	9.6	5.4	6.7	17.6
IV	Developed Basins in the AMR	5	7.9	9.3	3.4	5.9	13.8
V	AMR Basins with Streams on Main Sewage Line	5	10.0	10.5	2.1	9.0	14.1
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	19.8	19.0	2.1	16.6	20.5
VII	Sewage Effluent	2	-----	57.6	9.5	40.9	50.4

Table 4
Summary of Chemical Data by Groups (continued)

Potassium (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	1.3	1.2	0.5	0.5	2.1
II	Chattahoochee River	9	2.3	2.4	0.8	1.3	3.7
III	Semi-Developed Basins	7	2.3	2.6	1.7	1.0	5.7
IV	Developed Basins in the AMR	5	2.5	2.6	0.2	2.3	2.8
V	AMR Basins with Streams on Main Sewage Line	5	2.7	2.7	0.4	2.5	3.3
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	4.7	4.9	0.5	4.5	5.4
VII	Sewage Effluent	2	------	9.3	2.1	7.8	10.7
Dissolved Silica (values in mg/L)							
Group	**Description**	**No.**	**Median**	**Mean**	**Standard Deviation**	**Low**	**High**
I	Rural Streams	8	10	10	2	6	13
II	Chattahoochee River	9	7	7	1	5	9
III	Semi-Developed Basins	7	13	13	2	11	15
IV	Developed Basins in the AMR	5	13	14	2	12	17
V	AMR Basins with Streams on Main Sewage Line	5	17	16	3	13	19
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	13	18	7	13	26
VII	Sewage Effluent	2	-----	13	1	12	14

Table 4
Summary of Chemical Data by Groups (continued)

Total Dissolved Solids (mg/L)							
Group	**Description**	**No**	**Median**	**Mean**	**Std. Dev.**	**Low**	**High**
I	Rural Streams	8	38.9	43.7	10.4	16.1	58.4
II	Chattahoochee River	9	63.7	60.8	24.3	31.4	106.6
III	Semi-Developed Basins	7	84.9	90.8	26.5	65.8	138.3
IV	Developed Basins in the AMR	5	96.1	100.5	16.8	82.1	123.7
V	AMR Basins with Streams on Main Sewage Line	5	118.6	117.5	12.4	106.2	136.3
VI	Combined Sewage Overflow Basins/Basins Receiving Treated Effluent	3	192.2	198.9	34.9	167.9	236.7
VII	Sewage Effluent	2	------	296.7	65.3	250.5	342.9

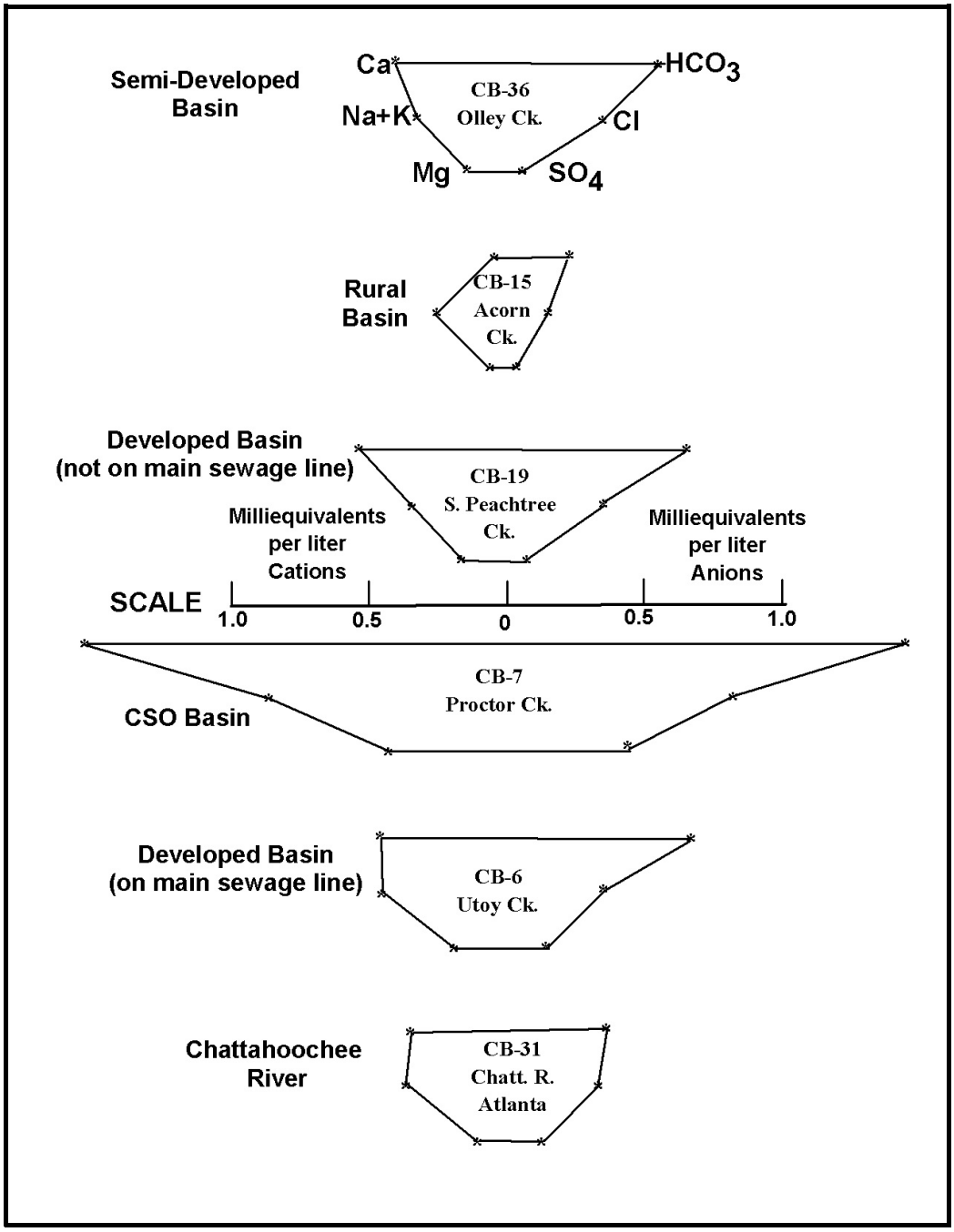

Figure 4. "Stiff" Diagrams for representative samples. Diagrams show relative proportions of cations and anions (in meq/L) for selected samples. See top polygon for position of ions.

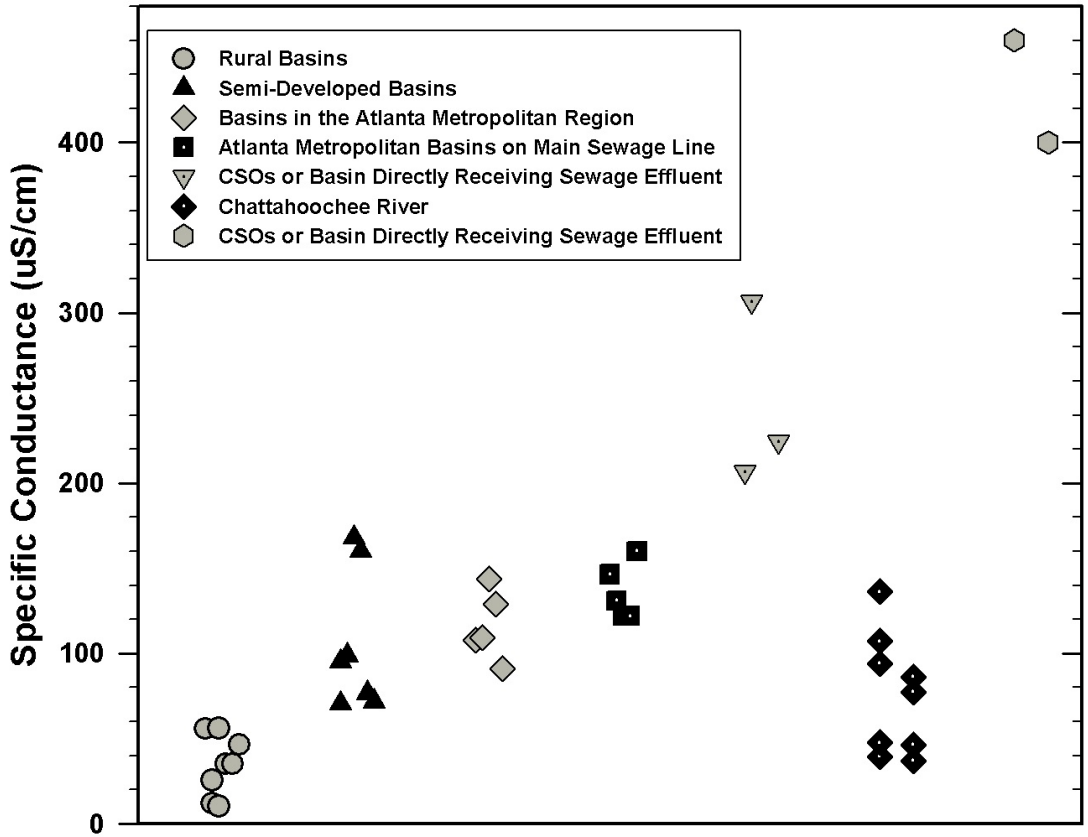

Figure5. Specific Conductance values for the various groups of waters

also the most concentrated within the sewage-impacted CSO basins (Figure 4) and within the sewage effluent itself (mean alkalinity = 110.4 mg/L; Table 4). Bicarbonate alkalinity averaged ~12 mg/L and were 3-4 times greater within base flow in the urban areas than in the rural streams, most likely indicative of a contaminant source for this ion. Comparative bicarbonate alkalinity concentrations for the various Chattahoochee basin sub-groups are shown in Figure 6 which shows similar trends to specific conductance (Figure 5).

Chloride and sulfate concentrations are also very revealing geochemical parameters within Chattahoochee Basin stream flow in that although both these ions can be derived from atmospheric and lithological sources, their presence in high concentrations is likely from an anthropogenic source. Chloride is a concentrated electrolyte in human wastes and is also present within household cleaning fluids. Sulfate can be derived from the oxidation of organic sulfur present in sewage wastes. The mean concentrations of chloride and sulfate within the two sewage effluent samples were 66.2 and 27.3 mg/L, respectively, compared to 5.4 and 1.9 mg/L within rural stream flow (Table 4 and Figure 5). In other words, waste water is approximately 13 times more concentrated with respect to sulfate and chloride than the more pristine waters found in the rural basins. Comparisons of sulfate within the urban waters are also revealing. Median sulfate concentrations were 2.4 greater for AMR basins adjacent to main sewage lines (Group V, Table 4) than urban basins *not* adjacent to the main sewage line (Group IV waters). The results for sulfate stands in contrast to bicarbonate, chloride, sodium, and TDS which were less than 1.3 greater in the *sewage line basins* than within the other developed AMR watersheds. Median sulfate concentrations in Group VI waters (CSO and sewage effluent-receiving basins) were >20 times more concentrated than in the rural basins (Table 4). In contrast, bicarbonate alkalinity, sodium, TDS, and chloride were only 5-7 times more concentrated in the Group VI than Group I (rural basin) waters. The median sulfate concentration within the Chattahoochee River base flow is 5.6 mg/L and ranges between1.8 and 10.4 mg/L; approximately twice as high as rural base flow but much lower than in most of the other urban basins (Table 4).

Sulfate and chloride concentrations for base flow within the various sub-groups of basins are shown on Figures 7 and 8. The sulfate and chloride concentrations (as well as specific conductance and other major ion concentrations) in Big Creek (at Cumming) base flow are quite elevated in relation to the other samples in this group (semi-developed basins outside of the Atlanta metropolitan basin; Group III, Table 4). The specific conductance of this sample (CB-22) was 168 µS/cm (Appendix 2), approximately 77% higher than median base flow for this group. The chloride concentration in this sample was 49 mg/L, clearly reflecting some waste contribution from sewage effluent disposal upstream of where the sample was taken. In short, these data show that base flow in basins outside of the AMR under some circumstances can become as contaminated or more contaminated than base flow in stream basins within the main metropolitan area.

The ternay diagrams shown on Figures 9 and 10 show the entire set of study area base flow samples grouped by their relative percentage equivalence of cations (Figure 9) and anions (Figure 10). These diagrams do not, however, give any specific information about the magnitude of solute concentrations within any of the samples. As can be observed on Figure 9, most of the base flow samples are either dominated by sodium or are a mixed sodium-calcium type. The rural basins and base flow from the Chattahoochee River tend to be more sodium-dominated and the CSO basins are more calcic. The bicarbonate ion comprises between 50-70% of the total equivalence of base

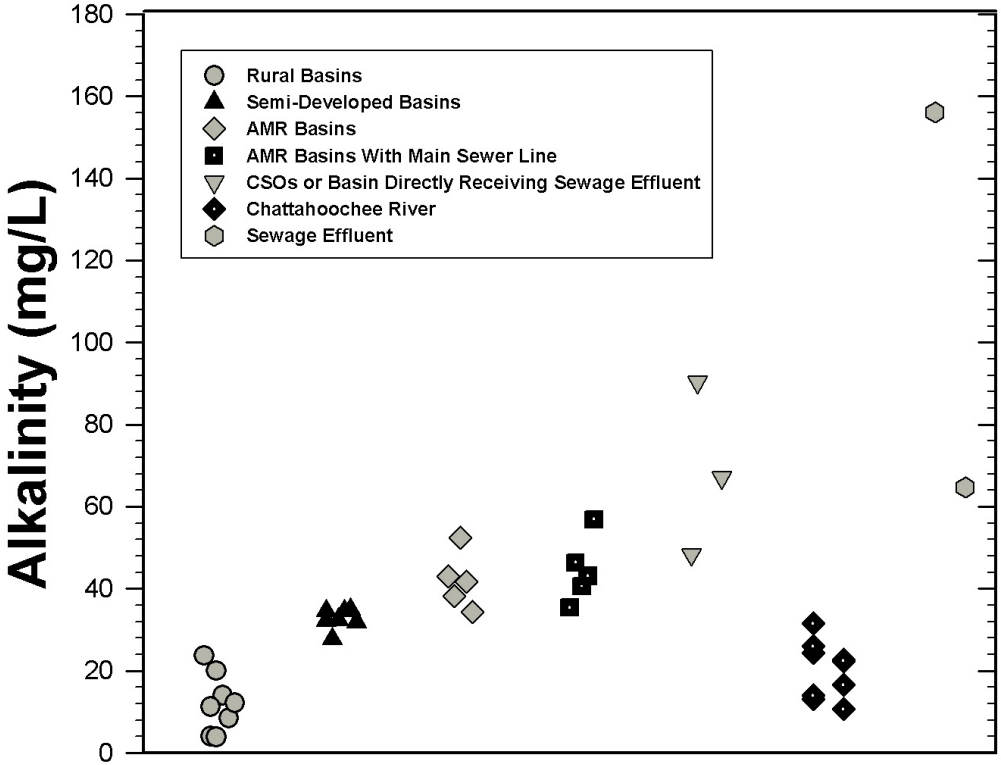

Figure 6. Alkalinity concentrations for the various groups of waters

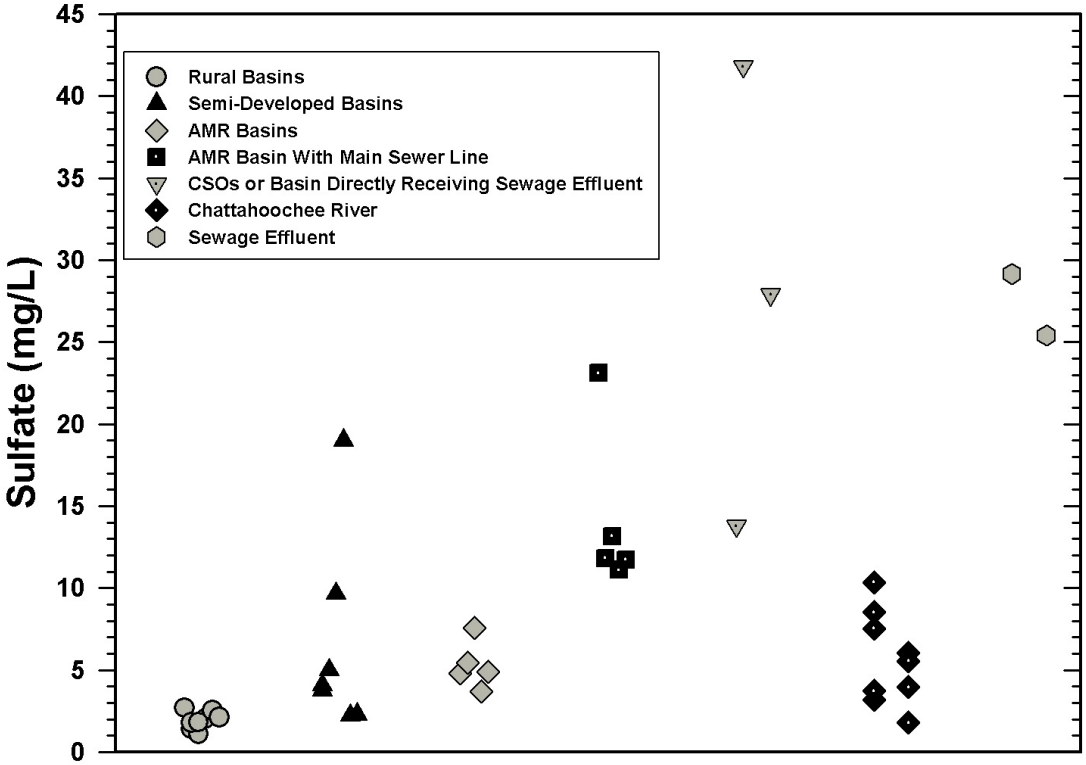

Figure 7. Sulfate concentrations for the various groups of waters

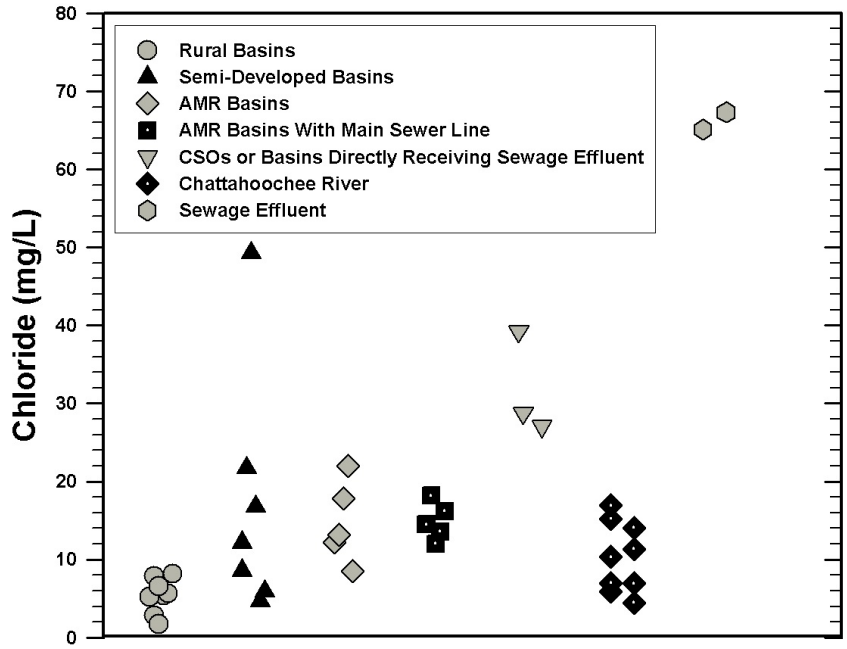

Figure 8. Chloride concentrations for the various groups of waters

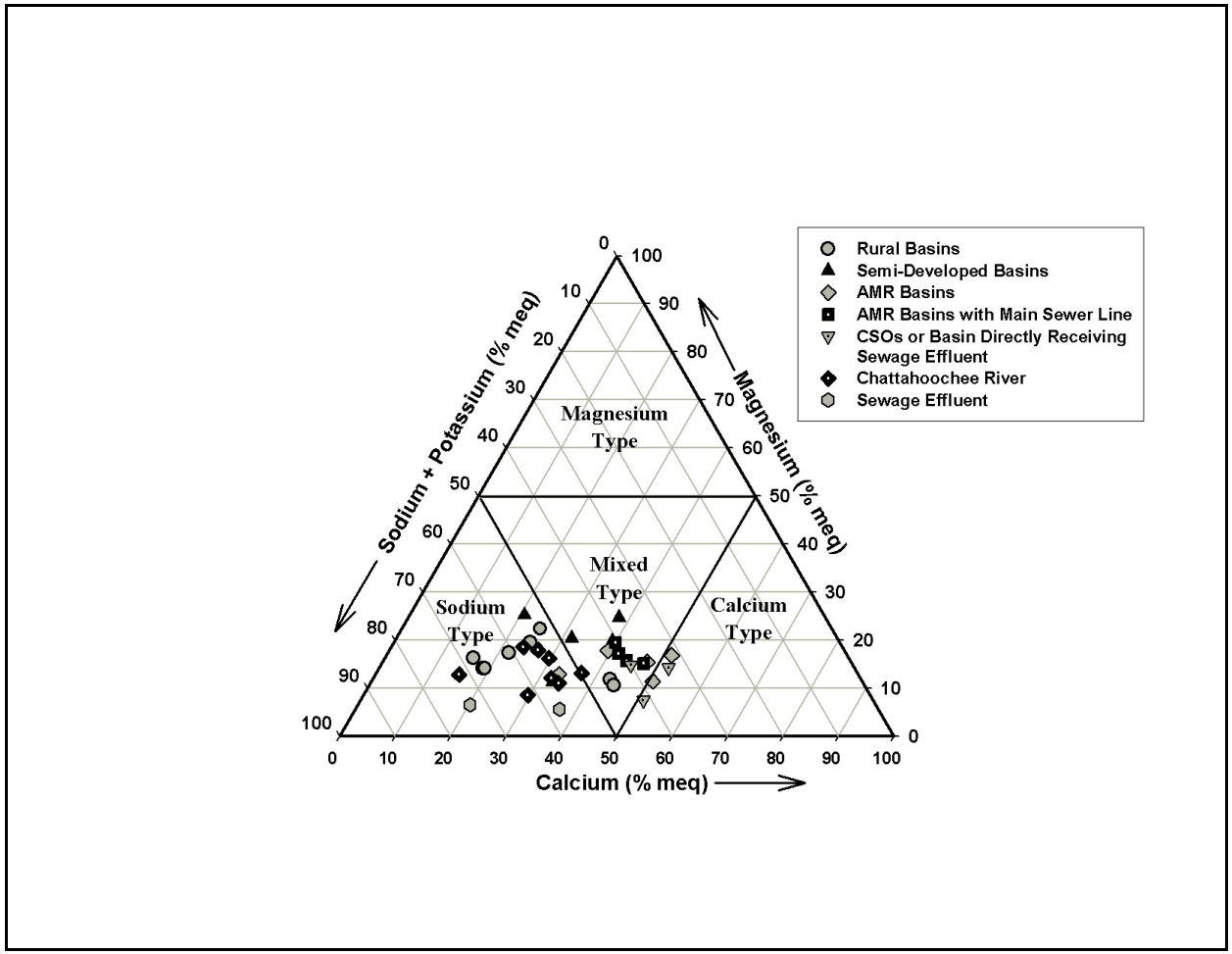

Figure 9. Ternary diagram showing the percentage of cations (in milliequivalents) for the various water groups

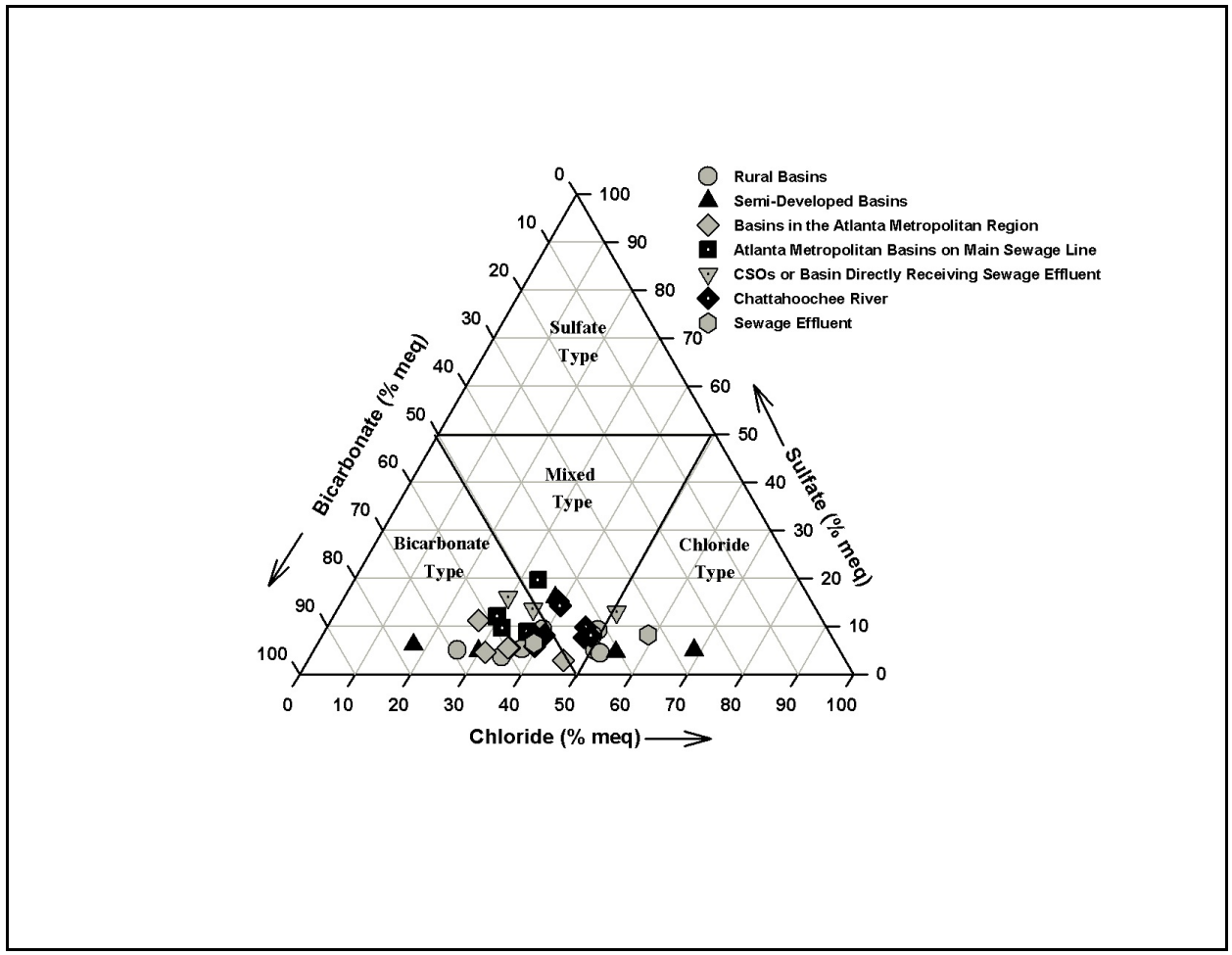

Figure 10. Ternary diagram showing the percentage of anions (in milliequivalents) for the various water groups

flow within the CRB and the chloride ion comprises between 30-40% of the total equivalence. It can also be deduced from Figure 10 that although the percentage of sulfate by equivalence is low (i.e. < 20%) in all of the base flow, there is a higher percentage of sulfate in those basins either on the main sewer line and those associated with CSO facilities.

Statistical Comparisons: T-tests were employed for a more statistically rigorous comparison of the major ion geochemistry of the sub-groups of Chattahoochee River stream basins that were designated within this study. The sets that were defined for the t-tests (summarized in Table 5) were slightly different but closely resembled the previously described sub-groups listed in Table 1. A 95% confidence interval ($\alpha = 0.05$) was used as the significance level to base a decision as to whether the mean of one population or group was greater than another group (i.e. Populations "A" and "B" on Table 5). However, in most cases the degree of statistical confidence associated with these tests is much greater than this 95% confidence interval.

In all cases (i.e. for specific conductance, alkalinity, chloride, sulfate, sodium, potassium, and strontium {which will be discussed later}) the urban and semi-developed basin base flow is characterized by significantly higher solute concentrations than the rural streams. Likewise, in all cases the four Chattahoochee River base flow samples collected downstream of Atlanta were characterized by greater mean concentrations of solutes than the four Chattahoochee River locations upstream of the AMR (these trends will be discussed further in the next section). The comparisons between urban (n = 5) versus the semi-developed basins (n=7) are not as clear or uniform. Mean specific conductance, alkalinity, and sulfate concentrations were greater in the urban base flow; however chloride, sodium and potassium concentrations (all parameters associated with sewage effluent) were not significantly greater in the urban population than within the non-urban population (Table 5). Similarly, the results of the t-tests between those basins located on the main sewage line in Atlanta versus those Atlanta basins that were not on the main lines were also mixed. Chloride and alkalinity concentrations were *not* significantly greater in base flow for those stream basins located on the main sewer line than those off the main line (Table 5). Sulfate concentrations were significantly greater in the urban base flow than in the non-urban base flow and greater in the urban basins with the main sewer lines than those without main sewer lines. Perhaps this indicates that sulfate is the most revealing indicator of sewage effluent impacts upon stream water chemistry. Nonetheless, the results are mixed and do not provide totally definitive evidence that Atlanta's aged sewage conveyance infrastructure is a source of ground water (base flow) contamination.

Major Ion Geochemical Trends Within Base Flow in the Chattahoochee River: Nine base flow samples from the Chattahoochee River upstream, downstream, and within the Atlanta region were chosen for this analysis (see Appendix 1 and Table 1). This corresponded to ~260 river kilometers (160 miles) and a watershed area of approximately 6,900 km^2 (or 2,660 mi^2) and extends from Helen to Franklin, Georgia. It was previously shown that concentrations of many of the major ion parameters within Chattahoochee River base flow more closely resemble "natural" or "background" concentrations than they do base flow sampled from the urban tributaries. In fact base flow from the Chattahoochee River closely resembles the chemistry of many of the major rivers of the world including the Ganges, Nile and Mississippi River. This is shown on Figure 10 which is known as a "Gibbs diagram" (after Gibbs, 1970 and Berner and Berner, 1987). The total dissolved

Table 5
Summary of T-Test Results for Key Geochemical Parameters in the Chattahoochee River Basin

Population A[1]	Population B[1]	Specific Conduct.	Alkalinity	Cl	SO_4	Na	K	Sr
Urban[3]	Rural[4]	S[2]	S	S	S	S	S	S
Semi-Developed[5]	Rural	S	S	S	S	S	S	S
Urban	Semi-Developed	S	S	NS[2]	S	NS	NS	S
Urban Basins on Main Sewage Line[6]	Urban Basins not on Main Sewage Line[7]	S	NS	NS	S	S	S	S
Chattahoochee River [8] (downstream of Atlanta)	Chattahoochee River [9] (upstream of Atlanta)	S	S	S	S	S	S	S

[1] Population "A:" has the greater mean value for the seven parameters than Population "B"

[2] "S" indicates positive T-test results; Means for populations A and B for the given parameter are significantly different from one another, at a 95% confidence interval or greater; "NS" = population means are not significantly different

[3] Urban Stream Basin Sites [n = 10]: CB-4, CB-5, CB-6, CB-8, CB-9, CB-10, CB-12, CB-13, CB-29, CB-33 (set does not include CSO basin)

[4] Rural Stream Basin Sites [n=8]: CB-1, CB-2, CB-15, CB-16, CB-18, CB-20, CB-23,CB-24

[5] Semi-Developed Basin Sites [n=7]: CB-3, CB-21, CB-22,CB-37, CB-34,CB-35,CB-36

[6] Urban Basins on Main Sewage Line Sites [n=5]: CB-4,CB-5,CB-6,CB-12,CB-13

[7] Urban Basins not on Main Sewage Line Sites [n=5]: CB-8,CB-9,CB-10,CB-29,CB-33

[8] Chattahoochee River (downstream of Atlanta) Sites [n=4]: CB-14,CB-17,CB-19,CB-30,CB-31

[9] Chattahoochee River (upstream of Atlanta) [n=4]: CB-1,CB-25, CB-26, CB-28

solids concentrations within the Chattahoochee River water samples average ~ 70 mg/L (slightly less than most of the other "rock weathering dominated" rivers shown on Figure 11); however, Chattahoochee River base flow apparently has a higher Na/Na+Ca ratio than the other major rivers that are "weathering dominated". The reason for this is not totally understood; however, it may be due to the negligible contribution of calcic minerals (e.g. calcite in limestones) within this aluminosilicate terrain and/or an additional input of sodium from a possible anthropogenic source.

As previously shown by the t-test analyses (Table 5), major ion concentrations in Chattahoochee River base flow downstream of Atlanta , while still relatively dilute, are greater than upstream of the Atlanta metropolitan reigon. The specific conductance, sulfate and chloride profiles on Figures 12, 13, and 14 show that solute concentrations in base flow increase by approximately a factor of three downstream of Lake Lanier (i.e. the upstream boundary of the AMR). Solute concentrations remain very low from the Blue Ridge mountain headwaters to the Buford dam in these relatively undeveloped headwater basins (i.e. $[SO_4]$ and [Cl] < 7 mg/L). Solute concentrations increase markedly within the AMR particularly between the Roswell area and the core metropolitan region around Atlanta. Specific conductance, chloride and sulfate concentrations decline by approximately 30-40% downstream of the AMR as the urban component of river base flow becomes "diluted" by a contribution from the rural basins south of and the relatively undeveloped basins west of the AMR. However, solute concentrations do not return to their upstream "background" levels (i.e. specific conductance ≈ 40 μS/cm) because there is not enough rural basin area downstream of Atlanta to generate sufficient runoff to accomplish this dilution.

Comparative Regression Analyses: Standard linear regression analyses were performed for the major ions, aqueous silica, strontium ion and strontium isotope ratios (which will be discussed later) on the 39 samples taken as part of this study (36 CRB base flow samples, two sewage effluent samples and one South River base flow sample). The linear regression coefficients (r^2 values) between each of the parameters were placed in a regression matrix (Table 6) to facilitate comparisons. Another comparative regression table (Table 7) summarizes similarly derived regression coefficients for the major ions within base flow from 32 stream samples derived from previous studies of the Flint, Oconee, and Ocmulgee basins (Rose, unpublished data and Rose, 2002). These basins are located generally no greater than 150 kilometers from Atlanta and samples were deliberately taken from relatively undeveloped parts of these basins located within the southern Georgia Piedmont Province.

The highest correlations (r^2 values > 0.80) for the Chattahoochee Basin base flow (Table 6) were between sodium and potassium, sodium and chloride, and potassium and chloride. A second group of relatively high regression coefficients ($0.60 < r^2 < 0.79$)were between calcium and bicarbonate, calcium and sulfate, potassium and bicarbonate, and sulfate and bicarbonate. These results are initially hard to explain in that one would expect to find the highest correlations between sodium and bicarbonate, sodium and calcium, calcium and bicarbonate in aluminosilicate watersheds. These high correlations would result from the *incongruent* or partial dissolution of

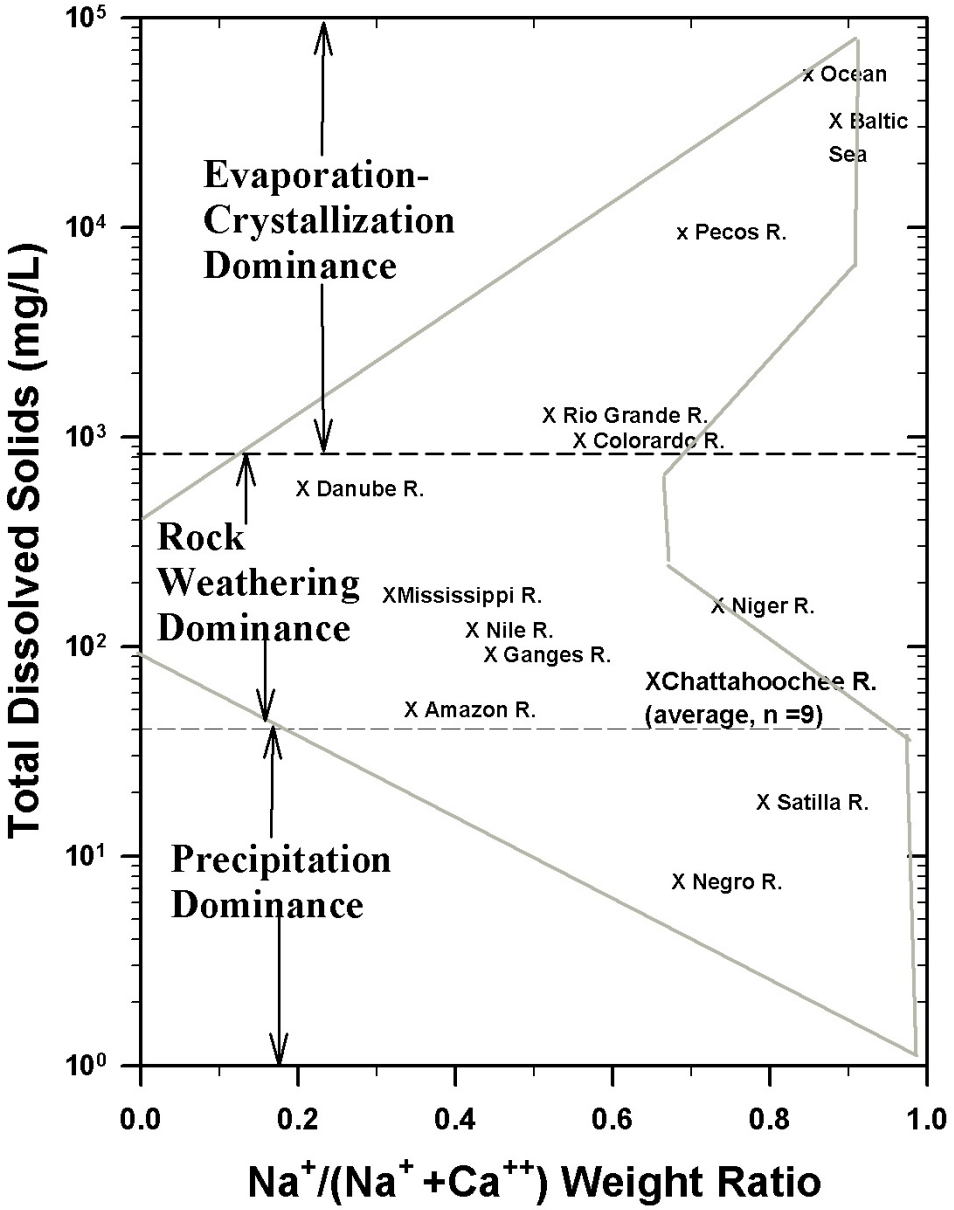

Figure 11. Gibbs Diagram showing comparison of the hydrochemistry of the Chattahoochee River with other rivers

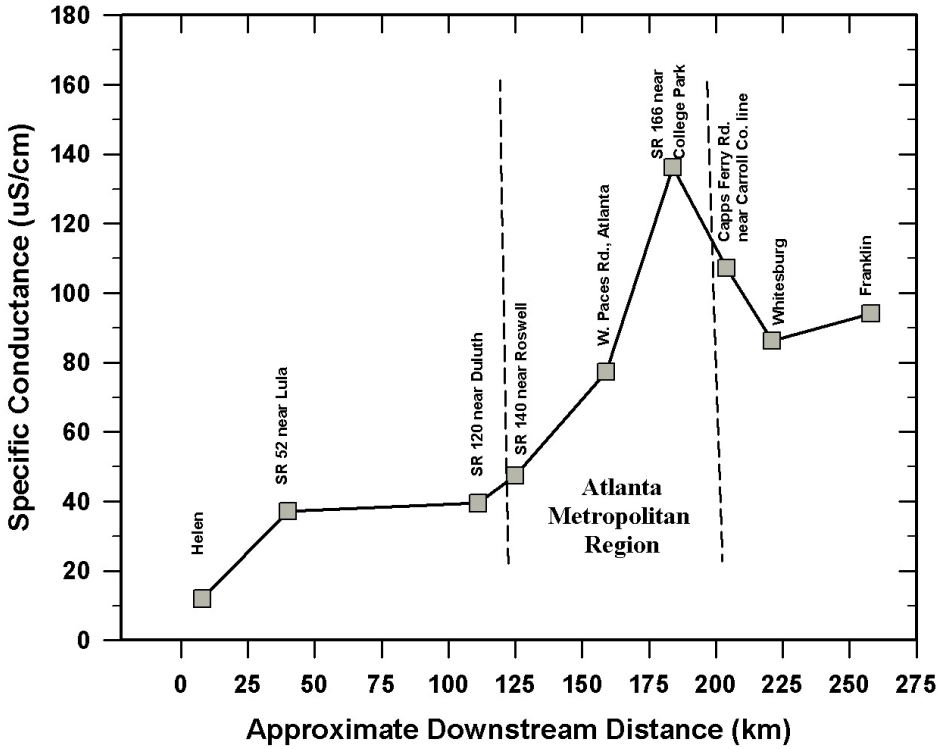

Figure 12. Profile of specific conductance within the Chattahoochee River

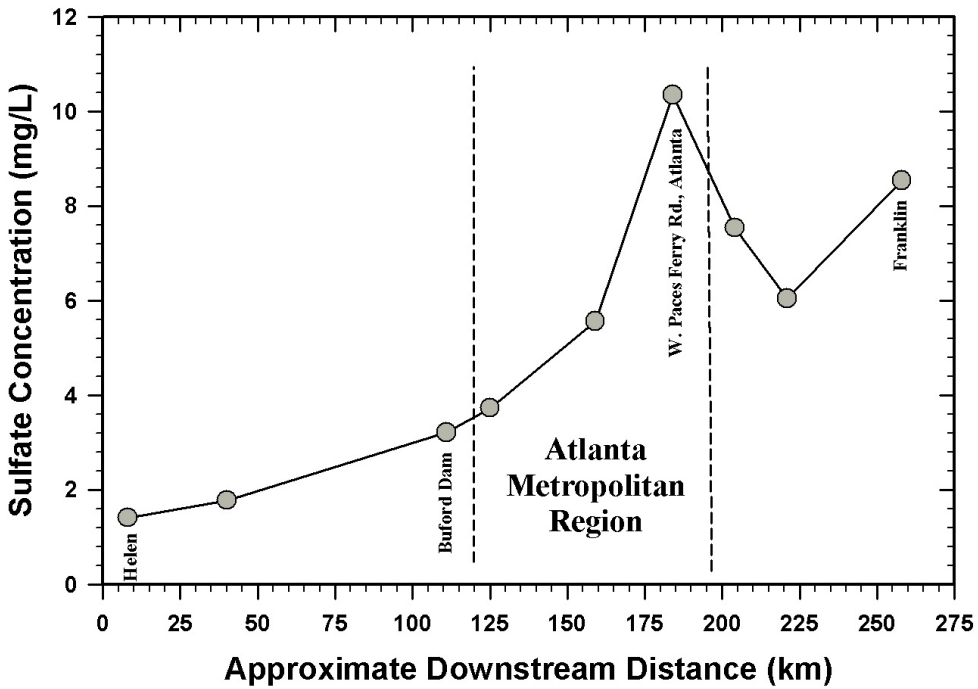

Figure 13. Profile of sulfate concentrations within the Chattahoochee River

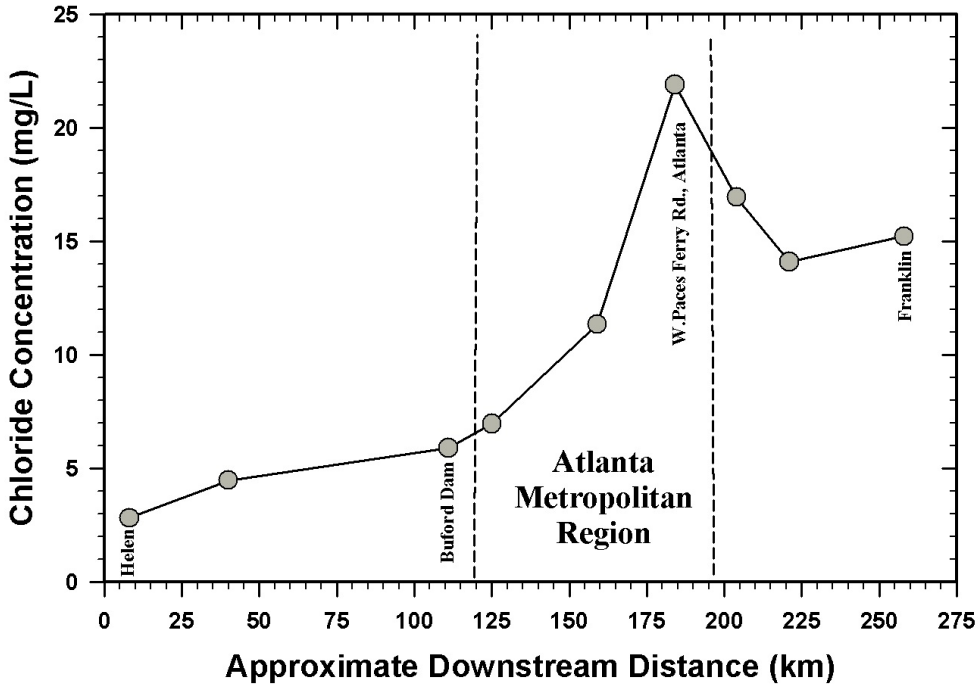

Figure 14. Profile of chloride concentrations within the Chattahoochee River

plagioclase feldspar minerals, biotite, and hornblende which dominate the normal weathering assemblage within Piedmont rocks and soils. The fact that bicarbonate did not appear in the group of highest correlation coefficients is also revealing in that is the dominant ion within Piedmont base flow. These results likely indicate that there is some source in addition to mineral dissolution that serves as a control upon base flow major ion variation.

A probable relationship between sodium, potassium, and chloride is that they are prominent human electrolytes and are therefore concentrated in human wastes (as can be inferred from the major ion chemistry of samples from the sewage effluent (samples WTP-1 and WTP-2) and the South River (Sample SR-1,which receives treated effluent from the Snapfinger Advanced Wastewater Treatment Plant in southeastern Dekalb Co). The potassium concentration in the untreated effluent (WTP-1) was 10.7 mg/L (Appendix 1) which is approximately 10-20 times higher than "background" concentrations in the rural CRB streams. The high degree of correlation between the waste-related ions (Na, K, and Cl) are a basin-wide phenomenon even though there is not a direct input of untreated or treated sewage wastes directly associated with most of the sampling locations. Eliminating data for the two waste treatment plants and the South River lower the regression coefficients somewhat, yet the Na/Cl, Na/K, and K/CL are still high ($r^2 = 0.69$, 0.76 and 0.82, respectively). The relatively high degree of correlation ($r^2 = 0.60$) between sulfate and bicarbonate may be related to their mutual presence in sewage waste; however, the degree of correlation between Ca and SO_4 ($r^2 = 0.69$) is more difficult to explain. The high degree of correlation ($r^2 = 0.73$) between Ca/HCO_3 might be related to mineral weathering.

The correlation coefficient matrix for the major ions in the relatively dilute base flow (see Rose, 2002) for the 32 base flow samples taken from the Flint, Ocmulgee basins is much different than the results for the CRB (Table 7). The regression coefficients were generally lower and the highest values ($0.65 < r^2 < 0.75$) were between Na/Ca, Na/HCO3, Ca/Cl, and Ca/SO4. Potassium (K) is not represented in this group and the regression coefficients for K/Cl, Na/Cl, and Na/K were relatively low ($r^2 < 0.50$) compared to those calculated for the Chattahoochee River Basin ($r^2 > 0.69$). In short, the correlations interpreted as being reflective of waste water (human electrolytes and cleaning solvents concentrated in sewage effluent) were not nearly as strong in the water samples form the relatively rural Flint, Ocmulgee, and Oconee basins. The high Na/Ca and Na/HCO_3 correlations for these rural basins were likely related to normal rock weathering; however, the Ca/Cl and Ca/SO_4 correlations are not as well understood. In short, the regression matrices (Tables 6 and 7) for the two different Piedmont Province base flow data sets are quite different and provide evidence of the human impact upon water quality in the heavily urbanized Chattahoochee Basin.

Table 6
Major Ion Geochemistry of the Chattahoochee River Basin
Regression Coefficient (r^2)Correlation Matrix (n=39)

	Specific Cond.	Ca	Mg	Na	K	HCO_3	Cl	SO_4	H_4SiO_4	Sr	$^{87}Sr/^{86}Sr$
Specific Cond.	1.00	0.70	0.45	0.87	0.88	0.88	0.83	0.74	0.18	0.40	0.12
Ca		1.00	0.49	0.43	0.54	0.73	0.45	0.69	0.26	0.63	0.09
Mg			1.00	0.25	0.35	0.39	0.39	0.54	0.43	0.64	0.19
Na				1.00	0.81	0.55	0.87	0.51	0.07	0.18	0.09
K					1.00	0.70	0.90	0.53	0.07	0.21	0.10
HCO_3						1.00	0.55	0.60	0.23	0.43	0.14
Cl							1.00	0.46	0.08	0.17	0.09
SO_4								1.00	0.25	0.64	0.04
H_4SiO_4									1.00	0.63	0.11
Sr										1.00	0.13
$^{87}Sr/^{86}Sr$											1.00

Summary of Strongest Regression Coefficient Values for Ionic Parameters	
$r^2 > 0.80$	Na/K; Na/Cl; K/Cl
$0.60 < r^2 < 0.79$	Ca/HCO_3; Ca/SO_4; Ca/Sr; Mg/Sr; K/HCO_3; HCO_3/SO_4; SO_4/Sr

Table 7
Major Ion Geochemistry of the Oconee, Ocmulgee, and Flint River Basins
Regression Coefficient (r^2)Correlation Matrix (n=32)

	Ca	**Mg**	**Na**	**K**	**HCO_3**	**Cl**	**SO_4**
Ca	1.00	0.51	0.68	0.24	0.32	0.75	0.71
Mg		1.00	0.53	0.23	0.49	0.35	0.19
Na			1.00	0.29	0.70	0.50	0.26
K				1.00	0.19	0.35	0.07
HCO_3					1.00	0.13	0.01
Cl						1.00	0.58
SO_4							1.00
Summary of Strongest Regression Coefficient Values for Ionic Parameters							
$r^2 > 0.65$	Na/Ca, Ca/SO_4, Na/HCO_3, Ca/Cl						

Strontium Ion Concentrations and Strontium Isotope Ratios:

Comparison With Results From the Middle Oconee Basin: Strontium ion concentrations and strontium isotope ratios were measured in base flow and sewage effluent samples in order to determine if these parameters can provide useful information pertaining to the effects of land utilization and sewage waste disposal upon water quality within the study area. A necessary related objective of this analysis was to examine the correlations between Sr isotope ratios and the major ion concentrations. There was a wide range of both strontium concentrations [5.2 μg/L < Sr < 140.8 μg/L] and $^{87}Sr/^{86}Sr$ ratios [0.709460 < $^{87}Sr/^{86}Sr$ < 0.723274] as summarized in Tables 8 and 9. This is consistent with the variation observed with respect to the major ion geochemistry of the Chattahoochee River Basin.

The strontium data are only meaningful when analyzed on a comparative basis. As stated previously, a similar study of strontium isotope variation was undertaken in 2003-2004 within the rural Middle Oconee basin north of Athens, Georgia - approximately 50 miles east of the AMR (Rose, 2004 and Rose, 2005). Sr concentrations within the smaller (860 km^2) Middle Oconee basin varied only between 16.3-26.9 μg/L in base flow while $^{87}Sr/^{86}Sr$ ratios varied between 0.712595 and 0.717572. Recall that these ratios are significant to approximately the 6th decimal place and that the isotopic ratio at a given sampling location was virtually constant throughout the year. Both the Sr ion concentration and isotopic variation within the rural Middle Oconee Basin base flow is far less than the variation observed within the Chattahoochee basin samples acquired for this present study. The Middle Oconee Basin strontium isotope ratios variation was to third decimal place while the Chattahoochee River Basin ratios varied to the second decimal place. The two factors responsible for the relatively high degree variation (shown on Figure 15) within the Chattahoochee River Basin sample set are its far greater watershed area (with its related mineralogical diversity) and population density (with its attendant urban development).

Strontium Ion Variation within the Chattahoochee Basin: The regression matrices shown on Table 6 indicate that strontium ion concentrations correlate fairly well with the alkaline earth ions calcium (r^2 = 0.63) and magnesium (r^2 = 0.64). In comparison the correlations with the alkali ions sodium (r^2 = 0.18) and potassium (r^2 = 0.21) were considerably weaker. Strontium is an alkaline earth that can substitute for calcium and magnesium which are major elements in hornblende. This iron-rich aluminosilicate is one of the most important minerals that weathers in Piedmont watersheds (Burns et al., 2003). However, anthropogenic factors are likely necessary to account for the relatively high Sr ion concentrations (i.e. [Sr] > 30-50 μg/L) observed within base flow for many of the urban watersheds.

Strontium ion concentrations within CRB base flow vary strongly as a function of land use as can be inferred from the tight clustering of data with respect to each of the groups shown on Figure 15. Taking the extremes, the median strontium ion concentrations within the rural base flow and the CSO/effluent-impacted basins were 14 and 138 μg/L respectively (Table 9). Interestingly, median Sr concentrations were significantly higher within the CSO/sewage effluent- impacted basins (Proctor Creek, Clear Creek, and the South River) than within the effluent (75 μg/L) collected from the two waste treatment plants. The higher concentrations in the CSO-impacted stream basins may be the result of the combined input of strontium from mineralogical sources and waste water. Both mean and median Sr ion concentrations increase in the order of $[Sr]_{\text{rural basins}} < [Sr]_{\text{Chattahoochee River}} < [Sr]$

$_{\text{semi-developed basins}} < [Sr]_{\text{developed basins}} < [Sr]_{\text{basins along main sewage lines}} < [Sr]_{\text{basins impacted by CSOs and sewage effluent}}$. This is similar to the order observed for most of the major ions and it is the exact order that would be expected if waste water was a major control over Sr ion concentrations. The t-test results (Table 5) confirmed that these and other similar comparisons are statistically significant.

Strontium ion concentrations within the Chattahoochee River varied approximately between 20-40 μg/L and were generally lower than within the urban tributaries (Table 9). This variation closely (but not exactly) resembles river profiles for most of the major ion parameters including TDS and alkalinity concentrations. Strontium concentrations were lowest (<10-20 μg/L) in the Blue Ridge headwaters and then increased to greater than 40 μg/L in Chattahoochee River base flow within the AMR (Figure 16). Clearly the peak on Figure 16 coinciding with urban Atlanta portion of the Chattahoochee shows that Sr is strongly controlled by urban sources of this trace metal. Other metals such as lead and zinc show a strong *urban gradient* or influence as well within the Chattahoochee basin [Neumann et al. (2005); Rose et al. (2001); and Callendar and Rice (2000)].

The range of $^{87}Sr/^{86}Sr$ ratio variation (between 0.709460 - 0.723274) observed within Chattahoochee River basin base flow (Figure 15) is considered major for a watershed comprised only of metamorphic rock and aluminosilicate minerals. This range of variation which was significant to the second decimal place is far more common to mixed lithology watersheds where both silicate rocks which yeild relatively high $^{87}Sr/^{86}Sr$ ratios and carbonate rocks which yield relatively low ratios are present (McNutt et al., 1990; Bullen and Kendall, 1998; and Palmer and Edmond, 1992). A definitive explanation can not be given for the observed range of variation; however, it is possible that there is a trace volume of carbonate minerals present as vein material within these watersheds.

Strontium isotope ratios were generally greater in rural base flow (particularly upstream of the AMR) than in the other groups (Figure 17). This is apparent when examining Sr isotope ratios along the longitudinal profile of the Chattahoochee River (Figure 18) in which values decline from greater than 0.7160 upstream of the AMR to approximately 0.7120 in Chattahoochee River base flow within the metropolitan region. This may be the result of natural variation and/or may have some poorly understood anthropogenic cause. However, an explanation for these ratios can not be directly attributed to the imposition of waste water.

As shown on Table 9, the median isotopic ratio of the CSO/sewage impacted basins was 0.713958 which was intermediate between the rural streams (0.716989) and the semi-developed basins (0.710295). Median $^{87}Sr/^{86}Sr$ isotope ratios varied by group as follows (Table 9): $^{87/86}Sr_{\text{semi-developed basins}} < {}^{87/86}Sr_{\text{Chattahoochee River}} < {}^{87/86}Sr_{\text{developed basins}} < {}^{87/86}Sr_{\text{basins impacted by CSOs and treated waste water}} < {}^{87/86}Sr_{\text{basins along main sewage line}} < {}^{87/86}Sr_{\text{rural basins}}$. This is not the relationship observed for Sr ion concentrations and the relative magnitude of the isotopic ratios can not be directly associated with waste water input. Results of t-tests (similar to those shown on Table 5) confirm that there are no significant correlations between mean $^{87}Sr/^{86}Sr$ isotope ratios and Sr concentrations or major ion concentrations. The $^{87}Sr/^{86}Sr$ isotope variation can not be explained in terms of simple mixing between waste water and natural water. If this was the case than the base flow samples would fall on or nearly on a straight "mixing line" when $^{87}Sr/^{86}Sr$ ratios are plotted versus Sr ion concentrations or the inverse of Sr concentration. Clearly, there is no "straight line" relationship that can be inferred from Figure 19 (with the possible exception of the subset of Chattahoochee River samples) and therefore there

is little isotopic evidence to support the supposition that the strontium isotopic ratios resulted from the mixing of waste water and natural water.

Table 8
Summary of Strontium Ion Concentrations and $^{87}Sr/^{86}Sr$ Isotope Ratios

Sample No.	Stream/Treatment Plant Name	Strontium Concentration (μg/L)	$^{87}Sr/^{86}Sr$ Ratio	Percentage Error[(a)]
WTP-1	RN Clayton Treatment Plant	54.8	0.713090	0.0007
WTP-2	Utoy Creek Treatment Plant	64.8	0.712979	0.0006
SR-1	South River on Klondike Rd.	57.0	0.712079	0.0008
CB-1	Chattahoochee River north of Helen	5.8	0.723274	0.0009
CB-2	Smith Creek at Anna Ruby Falls	5.2	0.719390	0.0009
CB-3	Sweetwater Creek south of Austell	38.4	0.710295	0.0007
CB-4	S. Utoy Creek at Harbin Rd.	79.1	0.714059	0.0007
CB-5	N. Utoy Creek at Peyton Rd.	70.0	0.714626	0.0008
CB-6	Utoy Creek at Fulton Industrial Blvd.	77.4	0.712622	0.0007
CB-7	Proctor Creek at Hightower Rd. (CSO)	140.8	0.713958	0.0007
CB-8	Burnt Fork Creek at Decatur	58.3	0.713813	0.0006
CB-9	South Peachtree Creek at Hahn Woods	57.0	0.714582	0.0007
CB-10	North Peachtree Creek at Druid Hills Rd.	66.0	0.713532	0.0007
CB-11	Clear Creek at Monroe Drive (CSO)	138.4	0.714493	0.0007
CB-12	Nancy Creek at West Wesley Rd.	68.8	0.715748	0.0008
CB-13	Peachtree Creek at Northside Highway	74.9	0.714171	0.0007
CB-14	Chattahoochee River at Franklin	39.8	0.713103	0.0007
CB-15	Acorn Creek at Highway 5	18.8	0.717913	0.0008
CB-16	Snake Creek near Banning	12.5	0.722794	0.0008
CB-17	Chattahoochee River at Whiteseburg	30.5	0.713302	0.0007
CB-18	Dog River at Highway 166	22.8	0.719831	0.0007
CB-19	Chattahoochee River at Capps Ferry Rd.	33.7	0.713288	0.0007
CB-20	Pea Creek at Highway 70	30.7	0.713877	0.0007
CB-21	Big Creek near Roswell	41.3	0.713005	0.0007

Sample No.	Stream/Treatment Plant Name	Strontium Concentration (μg/L)	$^{87}Sr/^{86}Sr$ Ratio	Percentage Error[(a)]
CB-22	Big Creek near Cumming	37.5	0.713305	0.0008
CB-23	Chestatee River south of Dahlonega	15.3	0.716064	0.0008
CB-24	Bear Creek west of Highway 129	43.2	0.714476	0.0007
CB-25	Chattahoochee River at State Rd. 52	20.1	0.716116	0.0006
CB-26	Chattahoochee River at State Rd. 20	21.1	0.714486	0.0008
CB-27	Sewanee Creek at Highway 23	54.7	0.713682	0.0006
CB-28	Chattahoochee River near Duluth	26.3	0.714002	0.0006
CB-29	Crooked Creek near Norcross	65.7	0.712171	0.0007
CB-30	Chattahoochee River at Holcomb Bridge Rd.	24.0	0.714198	0.0008
CB-31	Chattahoochee River at West Paces Ferry Rd.	35.4	0.712612	0.0007
CB-32	Chattahoochee River near College Park	41.1	0.712789	0.0007
CB-33	Camp Creek near Campbellton	55.1	0.713124	0.0008
CB-34	Sweetwater Creek near Villa Rica	35. 5	0.711228	0.0006
CB-35	Lick Log Creek on State Road 92	33.9	0.709460	0.0008
CB-36	Oily Creek north of Austell	56.2	0.712327	0.0007

[(a)] Percentage errors indicate that the $^{87}Sr/^{86}Sr$ ratio is precise to the 6th decimal place

Table 9
Summary of Strontium Data by Groups

Strontium Concentrations (values in μg/L)							
Group	**Description**	**No**	**Median**	**Mean**	**Std. Dev.**	**Low**	**High**
I	Rural Streams	8	13.9	19.3	12.9	5.2	43.2
II	Chattahoochee River	9	30.5	30.2	7.8	20.1	41.1
III	Semi-Developed Basins	7	38.4	42.5	9.2	33.9	56.2
IV	Developed Basins	5	58.3	60.4	5.1	55.1	66.0
V	AMR Basins with Streams on Main Sewage Line	5	74.9	74.9	4.5	68.8	79.1
VI	Combined Sewage Overflow Basins/ Basins Receiving Treated Effluent	3	138.4	112.1	47.7	57.0	140.8
VII	Sewage Effluent	2	-----	59.8	7.1	54.8	64.8
Strontium Isotope Ratios ($^{87}Sr/^{86}Sr$)							
Group	**Description**	**No**	**Median**	**Mean**	**Std. Dev.**	**Low**	**High**
I	Rural Streams	8	0.716989	0.718452	0.003538	0.713877	0.723274
II	Chattahoochee River	9	0.713392	0.713776	0.001083	0.712612	0.716116
III	Semi-Developed Basins	7	0.710295	0.710295	0.001609	0.709460	0.712327
IV	Developed Basins	5	0.713532	0.713444	0.000889	0.712171	0.714852
V	AMR Basins with Streams on Main Sewage Line	5	0.714059	0.714236	0.001123	0.712622	0.715748
VI	Combined Sewage Overflow Basins/ Basins Receiving Treated Effluent	3	0.713958	0.713510	0.001268	0.712079	0.714493
VII	Sewage Effluent	2	-----	0.713035	0.000078	0.713090	0.712979

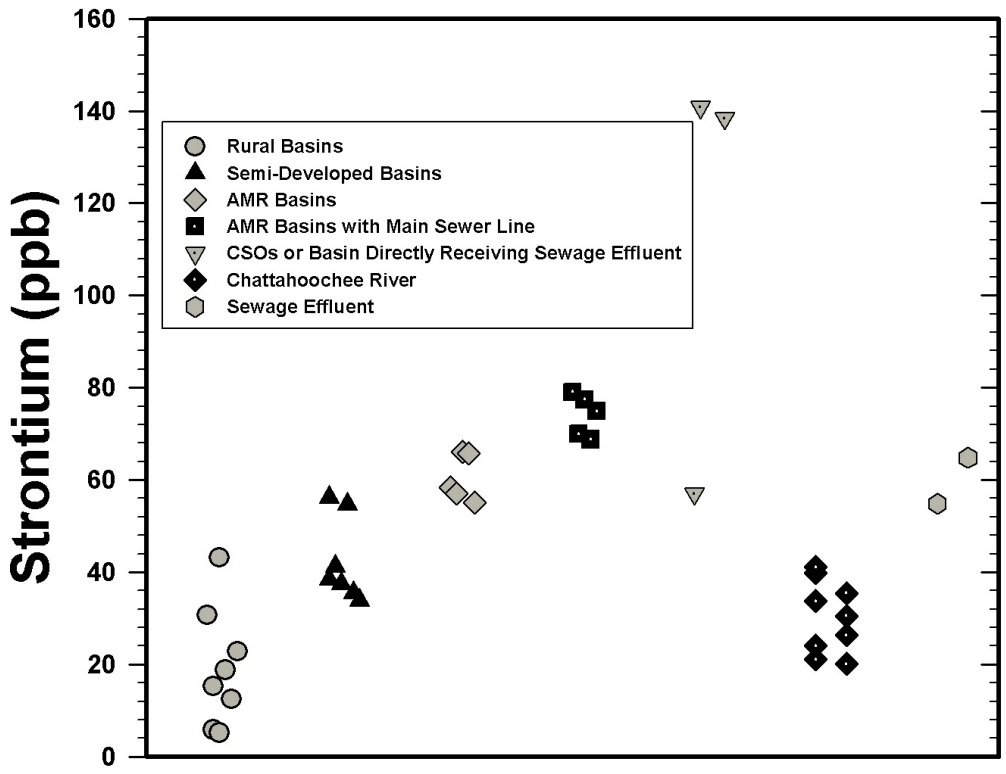

Figure 15: Strontium ion concentrations for the various groups

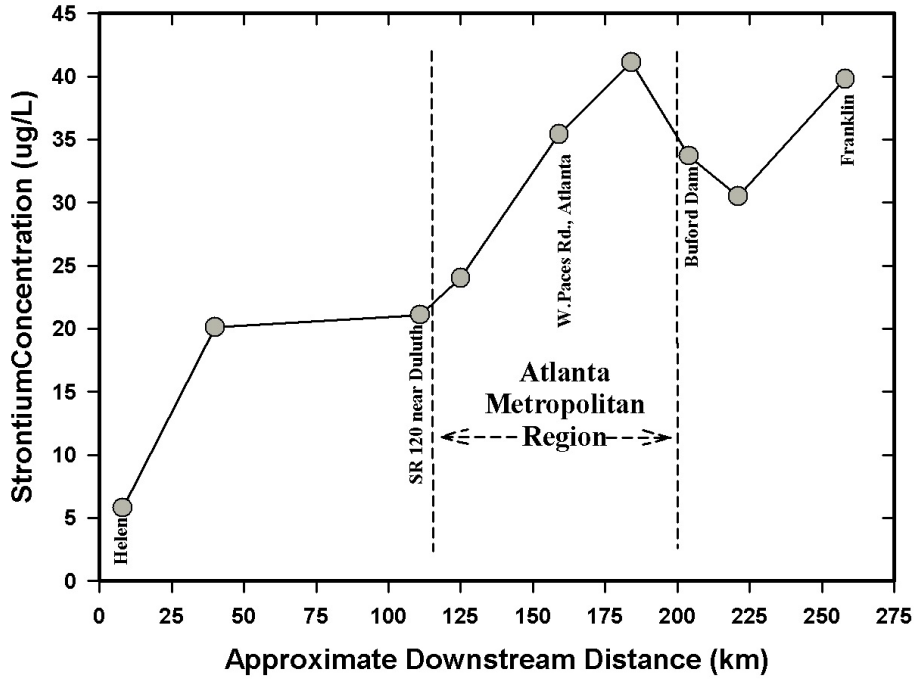

Figure 16. Profile of strontium ion concentrations within the Chattahoochee River

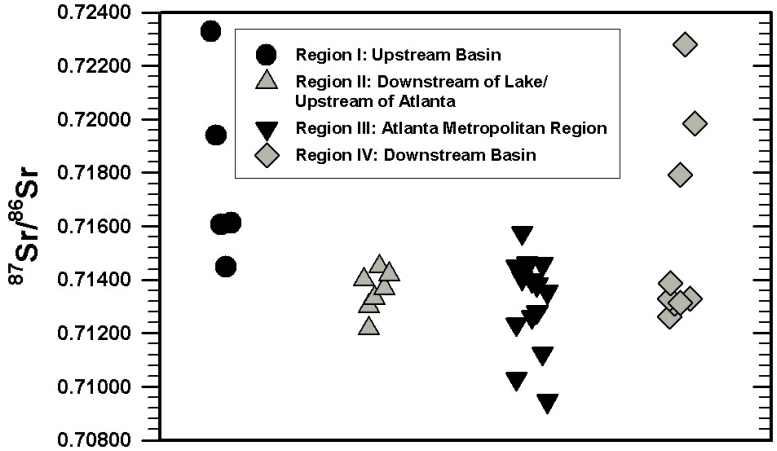

Figure 17: Strontium isotope ratios upstream, downstream, and within the AMR

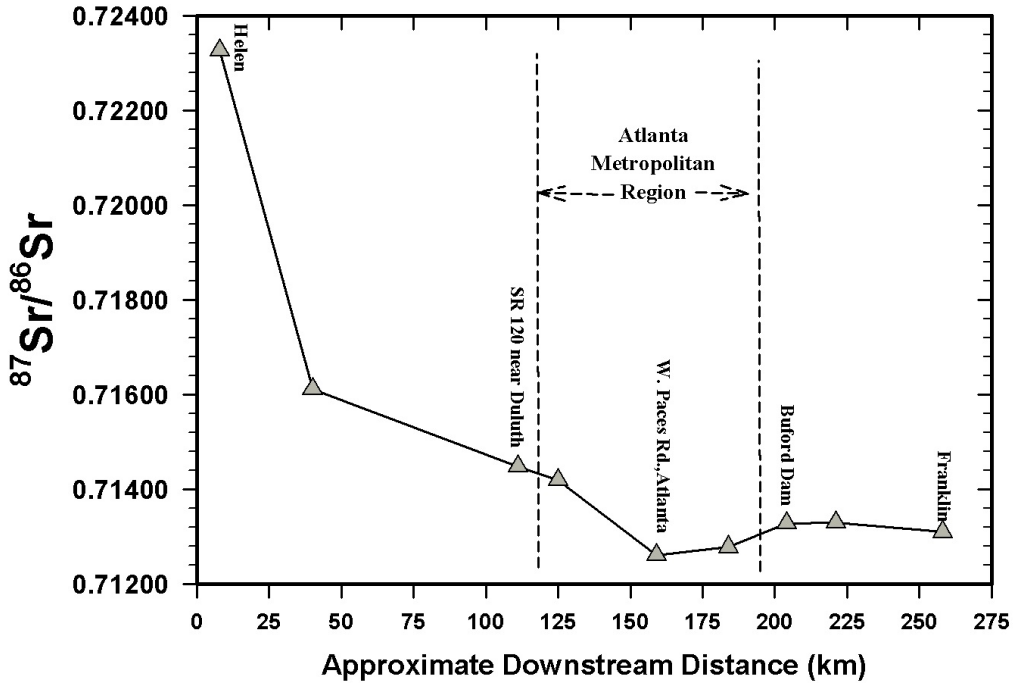

Figure 18: Profile of strontium isotope ratios within the Chattahoochee River

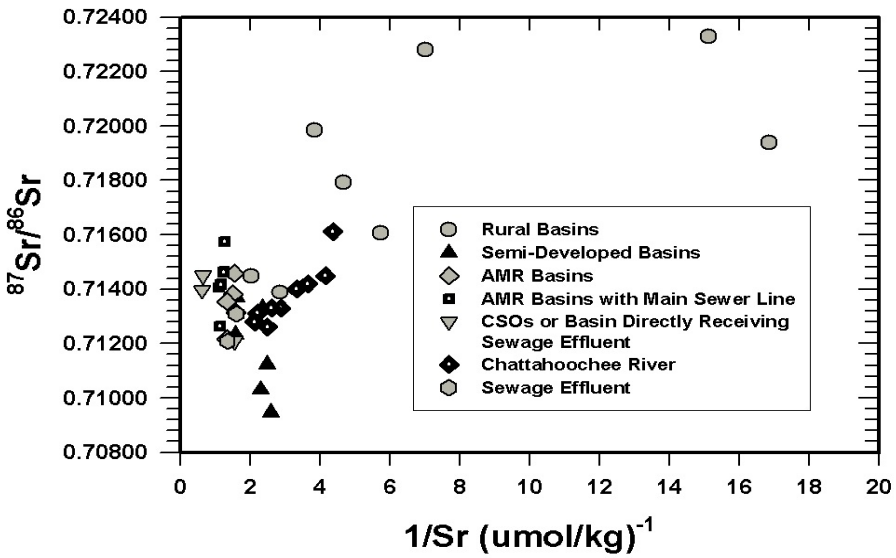

Figure 19: Plot of strontium isotope ratios versus inverse strontium ion concentrations (strontium mixing plot)

DISCUSSION

As previously stated, the major objective of this study was to determine whether strontium isotope ratios can be utilized to determine the effects of urbanization (particularly the effects of the aged sewage conveyance infrastructure of Atlanta) have upon the water quality of stream base flow within the Chattahoochee Basin. In order to accomplish this objective, a detailed comparative analyses of base flow chemistry was undertaken using data collected from approximately 40 sampling locations within the CRB. This may be the most comprehensive synoptic analysis of base flow chemistry within this study area to date and it represents a "pilot" study in this setting with regard to the use of strontium isotope ratios. The Chattahoochee basin with its large urban center and its highly diverse land use within a limited watershed area offers ample opportunities for this type of comparative hydrochemical analysis.

In order to facilitate a comparative analyses the sample set was divided into seven categories shown on Table 1that include: 1) rural basins (both upstream and downstream of the AMR); 2) semi-developed basins (i.e. those basins with a relatively low population basin outside of the highly developed inner core of the AMR); 3) basins in the AMR *not* containing a City of Atlanta main sewage line; 4) basins in the AMR in which the main stream parallels a City of Atlanta main sewage line; 5) basins in which a Combined Sewage Overflow [CSO] facility exists or a basin receiving treated sewage effluent; 6) nine sampling sites along a longitudinal profile of the Chattahoochee River (both upstream and downstream of the AMR); and 7) two sewage effluent samples. Any such subdivision admittedly has some arbitrary elements in that a given stream may not fit into any neat category. For example, Big Creek northwest of the AMR downstream of Cumming, GA (samples CB-21 and CB-22) has been designated as a "semi-developed" basin in that it is well upstream of the AMR; however it likely also receives some sewage effluent from a small upstream treatment plant. Another complication is that is possible that some of the urban basins designated in Group 3 may have a sewage conveyance infrastructure that is as damaged and leaks as much or more sewage into the subsurface than those basins designated on the main sewage line (Group 4). Nonetheless, the results from this analysis were in many ways revealing and are believed to reasonably represent major hydrochemical trends within the CRB.

The clearest finding of this study is that major ion concentrations are often two to four times higher in urbanized basins in the relatively undeveloped basins upstream and downstream of the AMR. The Chattahoochee Basin is underlain by aluminosilicate rocks which has only a limited solubility and when a basin is left within a relatively undisturbed state, total dissolved solid concentrations (TDS) are typically below 50 mg/L. Apparently any degree of basin development results in increased solute concentrations within the base flow component of stream flow. This is akin to saying that basin development results in some form of "ground-water contamination" or "ground-water perturbation"; however, the exact nature of this disturbance is not always clear and its causes and ontology are far more difficult to diagnose than pollution associated with storm water runoff. In most cases this added input of solute to ground water base flow associated with urbanization in the AMR can not be linked with any one point source in ground water nor can it be linked to any one obvious feature present on the earth's surface. The relatively low rate of base flow generation observed in urban basins may also be a contributing factor accounting for the relatively high solute concentrations observed in urban base flow.

The Chattahoochee River receives untreated sewage effluent in surface water runoff from various tributaries following heavy storms. Such occurrences are marked by the often dangerous influx of coliform bacteria within the storm runoff; however, it is not readily apparent what long-term impacts sewage effluent has on water quality within the CRB. It is not known whether this effluent seeps into the subsurface and if these salts are later "flushed" from the riparian zone in stream base flow. The influx of storm runoff into the subsurface (if this does occur) may be accompanied by other sources of sewage wastes including leaky underground pipes. In that the City of Atlanta has an aged infrastructure (which is currently being upgraded at great cost to local and federal tax payers) the influx of subsurface contamination from subsurface conveyance pipes would not be very surprising. Other possible sources of major ion solute contamination are the numerous septic tank systems that exist throughout the basin; however, this report has not addressed this issue. Simple land clearance and the application of fertilizer in the urban environment may also be another "non-point source disturbance" that has some long-term effect upon solute concentrations in base flow.

In addition to the problem of identifying non-point sources for potential subsurface contamination, there is the problem of determining which ions are diagnostic of sewage contamination in stream base flow. The analysis of untreated and treated sewage effluent from the R.N. Clayton and Utoy Creek facilities in metropolitan Atlanta and Snapfinger Creek facility in the South River basin greatly helped to facilitate these analyses. Sewage effluent is concentrated with respect to all the major ions. For example potassium which is the least concentrated of the major elements, is 5-10 times more concentrated in sewage effluent than within base flow from rural streams or the Chattahoochee River.

The most useful of the major ions to focus upon are chloride and sulfate. With the exception of evaporite mineral salts (e.g. halite, anhydrite, and gypsum), chloride and sulfate ions are not readily derived from rock-forming minerals. In that these evaporite salts are not commonly present within the CRB, the sources of chloride and sulfate are not from rock and soil minerals which contribute most of the solute load to non-contaminated base flow. Both chloride and sulfate can be atmospherically derived and then concentrated within the shallow subsurface by evaporation. However, this process does not typically result in inordinately elevated stream water concentrations as evidenced by the relatively low concentrations observed for these ions in rural base flow and within most of the semi-developed basins. Chloride is a major human metabolic electrolyte and therefore is a dominant ion in liquid wastes. Sulfate is likewise an electrolyte and is also derived from the oxidation of reduced sulfur compounds in organic wastes. Mean chloride and sulfate concentrations are approximately 12-14 times greater in sewage effluent than within base flow from rural CRB streams (Table 4). Hence, these two ions are believed to be the most diagnostic of waste influx to stream water. Alkalinity concentrations were also elevated in those waters which were concentrated with respect to sulfate and chloride (Figures 20 and 21). The elevated alkalinity concentrations may have in part resulted from breakdown of reduced sulfur molecules in organic waste which is known to produce high alkalinity concentrations within waste water.

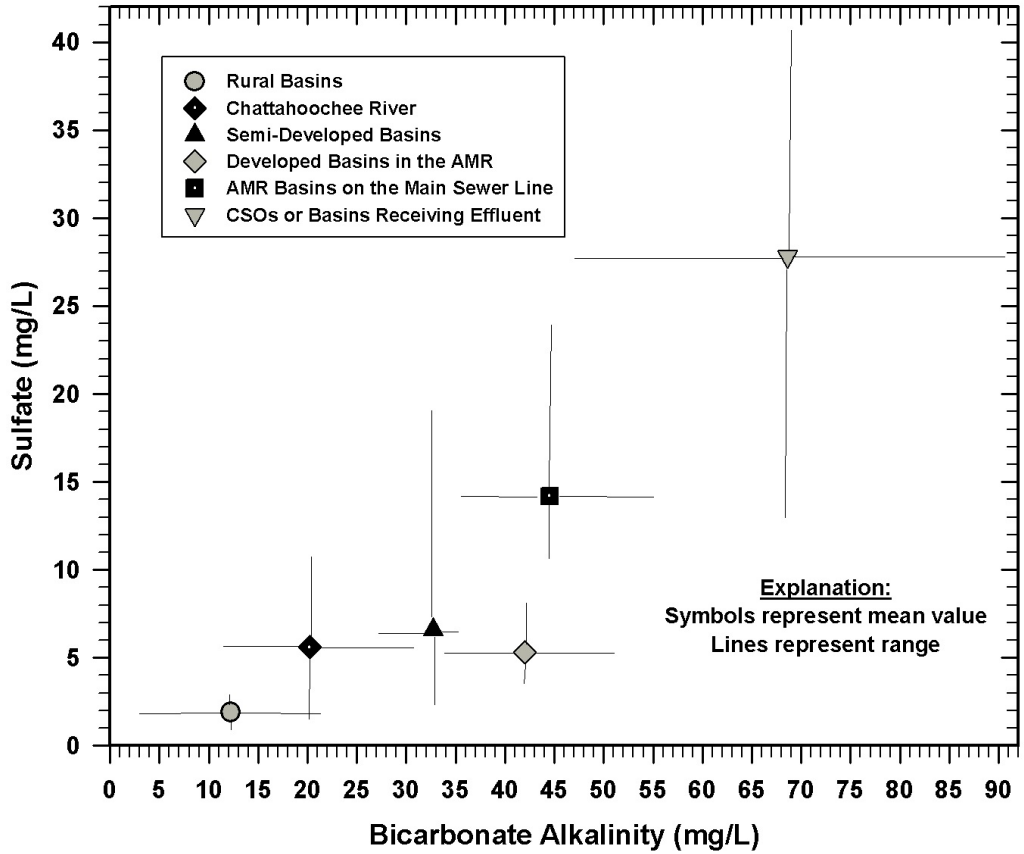

Figure 20: Plot of sulfate versus bicarbonate for various water groups showing ranges

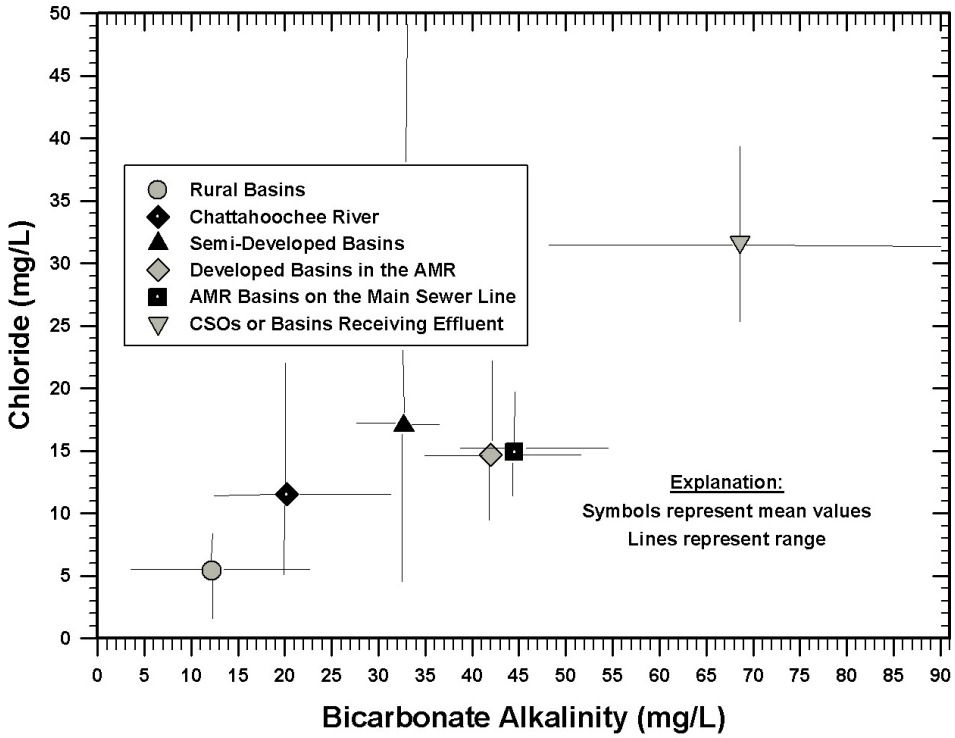

Figure 21: Plot of chloride versus bicarbonate for various water groups showing ranges

Clearly, all of the stream base flow within the AMR were characterized by chloride and sulfate concentrations that were significantly above "background" levels (i.e. concentrations found in rural streams). The high degree of correlation (as evidenced by least-square regression coefficients > 0.80) between potassium, sulfate, and chloride strongly suggests that there is an apparent basin-wide impact of human waste and sewage effluent. However, none of the streams with the possible exception of CSO basins and the South River (which directly receives large quantities of sewage effluent) were as polluted with chloride and sulfate as raw or treated sewage wastes (Figures 20 and 21). Sulfate concentrations within these three basins (samples SR-1, CB-7, and CB-11) equaled or exceeded those concentrations found in raw sewage. Raw sewage runs through these CSOs during periods of heavy storm flow (when sewage treatment facilities can not handle the combined storm and sewer flow) and it is likely that some of this sewage/storm water runoff mixture has seeped below the channels and/or through stream banks (i.e. in the riparian zone). During periods of base flow these salts are assumably "flushed" from the subsurface back into the stream channel, resulting in the extreme concentrations of alkalinity, chloride, and sulfate (Figures 20 through 23 and Table 4). Burns et al. (2003) in a study of a natural Piedmont watershed concluded that the riparian zone near the stream channel provides the most important source of solutes to stream flow within this setting.

This interpretation with respect to the contribution of salts from the near-stream zone around and below CSO facilities is consistent with the findings made by Burns et al. (2003) for the Panola Mountain Research Watershed facility. However, the origin for these relatively high concentrations of sewage-related salts observed in base flow is hypothetical and by no means represents a definitive explanation of the problem. In order to address this problem in a more rigorous manner, a ground water monitoring network (i.e. three-dimensional well "nests") would have to be installed in transects perpendicular to a stream channel in order to study the hydrogeochemistry of ground water flowing into the channel. It would be very difficult (but not impossible) to install such a network in most urban areas.

Definitive assessments of the effects of pollution upon base flow hydrochemistry of the other groups of basins that have been designated in this study are also problematic. One important inference that can be made from this study is that any degree of development within the ever-expanding AMR results in major ion concentrations that are substantially greater than those present within the base flow of rural streams. Sulfate and chloride concentrations are elevated by a factor of factor of approximately 3-4 within the semi-developed basins in the outlying sections of the AMR compared to those basins which have been designated as "rural". The explanation for these elevated salt concentrations is by no means certain; however, I speculate that there may be some low level of input resulting from septic tanks and sewer lines within the outlying regions.

Solute concentrations were generally greater within the urbanized base flow than in the semi-developed basins; however, this was not always the case (Figure 20 and 21). The same is true with respect to the comparison between solute concentrations between those AMR basins in which a main sewage line was present and its urban counterparts not underlain by a main sewage line. However, sulfate concentrations (but not chloride concentrations) were notably higher in base flow for those basins where a main sewage line was present than in the other urban streams (Figure 18 and 19). Therefore, a qualified argument based upon the elevated sulfate concentrations can be made that

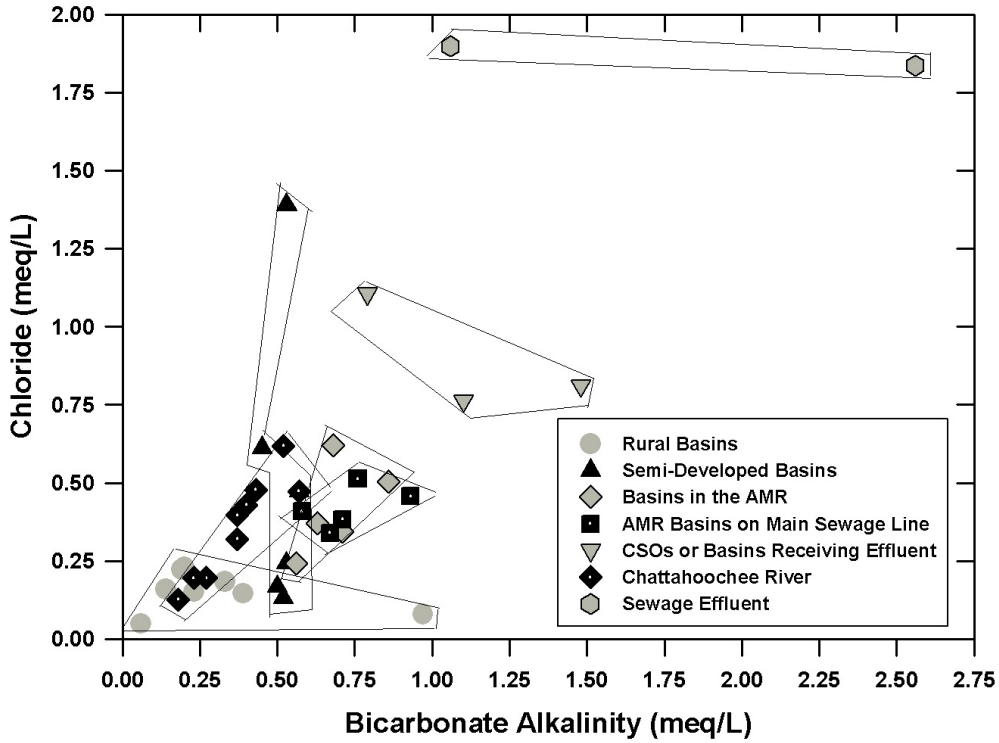

Figure 22. Chloride versus bicarbonate showing differences and similarities between various water groups

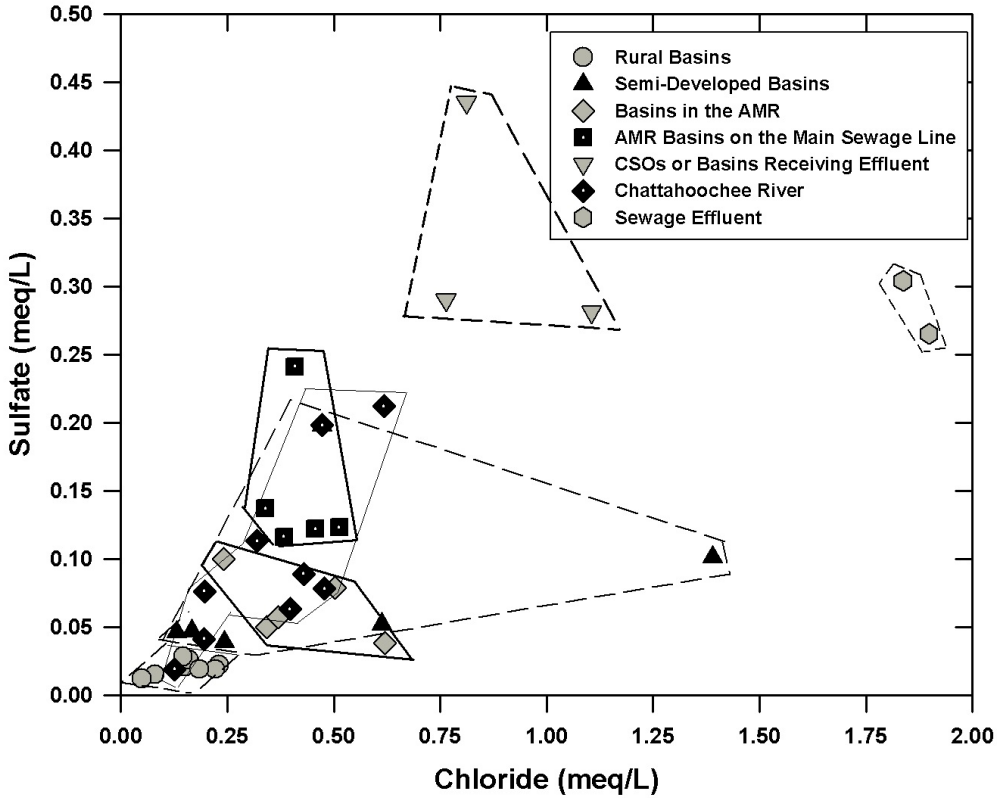

Figure 23. Sulfate versus chloride showing differences and similarities between various water groups

there is an impact from sewage pipes (possibly leaking within the subsurface) upon ground water and base flow hydrochemistry within the AMR. However, the evidence presented in this report is quite limited and the question should still be regarded as open.

There is a high degree of correlation between strontium ion concentrations and other solute concentrations and strontium is highly elevated within those basins that are most clearly impacted by sewage effluent. $^{87}Sr/^{86}Sr$ ratios vary greatly from basin to basin (variation is significant to the 2nd decimal place whereas the ratio can be measured precisely to the 5th or 6th decimal place); however, the variation is not systematic. Much of the variation is likely caused by mineralogical differences in the underlying rocks and soils of these basins; however, this has not been definitively established. The most important mineralogical factor would be the percent of rubidium-bearing minerals in that rubidium-87 produces strontium-87 through beta decay, thereby increasing the $^{87}Sr/^{86}Sr$ in water that has partially dissolved the rubidium-bearing minerals.

Although human wastes and cleaning solvents may have their own range of $^{87}Sr/^{86}Sr$ isotopic variation, there is no apparent strontium isotopic "signature" that can be definitively linked to sewage effluent within CRB base flow. One possible explanation is that the Sr isotopic ratios associated with sewage effluent are "masked" by natural lithological variation. This is suggested by the data associated with the rural basins in which the $^{87}Sr/^{86}Sr$ ratio varies between 0.713877 - 0.723274, encompassing most of the variation observed for the entire data set. In short, this research has clearly demonstrated "negative results" in that strontium isotope ratios can *not* be effectively used to assess the impacts of sewage effluent or other forms of contamination within base flow in urbanized basins. This present research has not, however, addressed the issue of whether these isotopic ratios can be used to assess the presence or wastes in storm runoff.

SUMMARY AND CONCLUSIONS

This study summarizes the results of a comprehensive synoptic investigation of the hydrochemical and isotopic composition of base flow within the upper 6,940 km^2 of the Chattahoochee River basin. Its most pressing concern was to determine what effects the imposition of sewage wastes and other urban contamination from the Atlanta Metropolitan Region (AMR) have upon the base flow hydrochemistry within the Chattahoochee River and its urbanized tributaries. Strontium ion concentrations, strontium isotope ratios, and the major ion chemistry were analyzed in ~40 diverse steam basins within the study area during the summer of 2005. The study took a comparative approach by subdividing the total sampling set into various sub-categories representing land use, population density and urban infrastructure placed on or near the stream basin (e.g. "CSOs" and "urban stream basins that parallel a main sewage line"). The major findings of this study are summarized as follows:

1) Runoff rates are approximately 520 mm (20 in) per year throughout most of the Piedmont portion of the Chattahoochee River Basin. This rate of runoff is approximately 40% of the annual rainfall (1320 mm or 52 inches) within this region of Georgia. Total runoff rates were slightly higher in Peachtree Creek, one of the of the most urbanized watersheds within the AMR, than elsewhere. Rates of base flow within the five CRB streams vary widely between 164-770 mm/year. This represents between 30-70% of the total yearly runoff. The relatively low rates of base flow

generation within urban basins might be a factor contributing to the increased solute concentrations observed within urban base flow.

2) Base flow in this region is characterized by stable oxygen isotope ($\delta^{18}O$) ratios that range from -6.10 to -3.47 per mil which increase gradually from north to south (i.e. downstream). $\delta^{18}O$ values increase in the Chattahoochee River from -5.8 per mil in the Blue Ridge headwaters to -4.0 per mil in Franklin, Georgia which was the most southern and downstream sampling point of the study area. This trend is congruent with latitudinal variation in weighted annual precipitation and strongly suggests that the base flow sampled as part of this study represents well-mixed annual precipitation averages. This is consistent with the tritium concentrations that average 7.6 T.U. indicating that base flow is comprised of a substantial component of ground water that has a subsurface residence times of several decades.

3) Strontium ion concentrations are highly elevated in those basins which sewage effluent likely affects the major ion chemistry of the streams; however, strontium isotope ($^{87}Sr/^{86}Sr$) ratios do *not* provide an adequate means for assessing the imposition of sewage waste effluent within this setting. This is likely because naturally occurring mineral weathering reactions impart a very wide range of isotopic variation ($0.709460 < {}^{87}Sr/^{86}Sr < 0.723274$) in stream base flow that encompasses and obscures any "waste signature" that might be present.

4) All major ion concentrations in base flow within all semi-urbanized and urbanized streams are greater than within rural basins both upstream and downstream of the Atlanta Metropolitan Region. Major ion concentrations within the Chattahoochee River increase as a result of influx from the AMR and remain elevated well downstream of the AMR. In general, there is a great diversity of water types and solute concentrations within the CRB and this variation is most likely more related to land use, population density, and sewage waste disposal activities than it is to natural lithological variation.

5) Major ion concentrations are most elevated in those stream basins that are most clearly impacted by waste water effluent including CSO facilities (Clear and Proctor Creek) and effluent disposal sites(South River). Solute concentrations are also typically greater within developed basins in the AMR than in the semi-developed basins north and west of Atlanta. There is less clear of a distinction with respect to the major ion chemistry between those AMR basins in which a main sewer line is present and those urbanized basins in which there is no main sewer line. However, sulfate concentrations are significantly greater in those basins such as Peachtree Creek which flow parallel to a main City of Atlanta sewer line.

6) Mean and median Sr ion concentrations in the order of $[Sr]_{\text{rural basins}} < [Sr]_{\text{Chattahoochee River}} < [Sr]_{\text{semi-developed basins}} < [Sr]_{\text{developed basins}} < [Sr]_{\text{basins along main sewage lines}} < [Sr]_{\text{basins impacted by CSOs and sewage effluent}}$. Interestingly, this is similar to the order observed for most of the major ions and it is the exact order that would be expected for an increasing contribution of contamination from sewage waste.

7) Apparently any degree of urbanization results in major ion concentrations that are elevated with respect to "background" (i.e. rural streams within the CRB). However, there is a wide range of variation and "overlap" associated with most of the major ion concentrations for the urbanized and

semi-urbanized subgroups designated in this study. This is the case for alkalinity, sulfate, and chloride concentrations which are associated with sewage waste.

8) Major ion and strontium ion concentrations within the Chattahoochee River are significantly greater downstream of the AMR than they are upstream of Lake Lanier. "Dilution" from the rural basins downstream of the AMR results in lower solute concentrations but is insufficient to negate the effects of pollutant influx from the AMR.

9) Regression analyses indicate that the highest major ion correlations within the CRB are between sodium, potassium, and chloride in the urban basins. This is not a common occurrence for stream water within the Georgia Piedmont Province as indicated by a comparative regression analysis of stream base flow from nearby rural streams within the Flint, Ocmulgee, and Oconee basins. The most likely origin for the elevated concentrations of sodium, potassium, chloride, sulfate, and alkalinity is sewage effluent in that these ions are concentrated in human electrolytes, household cleaning products, and the breakdown of organic molecules. The relatively high regression correlation coefficients (r^2 values > 0.69)for sodium, potassium, and chloride may indicate that waste water effluent has a basin-wide effect (at least downstream of Lake Lanier within the AMR).

10) An unequivocal origin of elevated solute concentrations within CRB base flow is far more difficult to identify than the elevated solute concentrations in surface water or storm water runoff. The most probable source of contamination is within the near-stream or riparian zone as evidenced by the high TDS, sulfate, potassium, chloride, and alkalinity concentrations observed in those river channels that were directly impacted by CSO facilities. One possible origin for these ions is the concentration of sewage-related salts in the subsurface (as a result of CSO discharges and/or leaky sewer lines). This inferred source is only speculative and would require detailed ground water investigations for confirmation. Other possible non-point sources of subsurface contamination are less obvious and can not be ruled out. These include septic tank effluent, fertilizer, and the infiltration of salts that may accumulate on disturbed land. However, these possible sources appear less likely and are far less understood than the input of sewage wastes to the shallow subsurface.

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Appendix 1: Description of Sampling Sites and Sample Inventory

Sample No.	Site	Sample Date	County	Description
WTP-1	RN Clayton Waste Water Treatment Plant	4/14/05	Fulton	Raw Sewage
CB-1	Chattahoochee R. north of Helen	4/21/05	White	Rural Blue Ridge headwater stream:
CB-2	Smith Ck.	4/21/05	White	Rural Blue Ridge headwater stream: 0.2 miles south of Ruby Falls
CB-3	Sweetwater Ck. south of Austell	5/9/05	Douglas	Semi-urbanized stream (AMR)[1]
CB-4	South Utoy Ck. @ Harbin Rd.	5/9/05	Fulton	Urbanized AMR stream on main sewer line
CB-5	North Utoy Ck @ Peyton Rd.	5/9/05	Fulton	Urbanized AMR stream on main sewer line
CB-6	Utoy Ck. @ Fulton Ind. Blvd.	5/9/05	Fulton	Urbanized AMR stream on main sewer line
CB-7	Proctor Ck. @ Hightower Rd.	5/9/05	Fulton	Urbanized AMR stream - downstream of CSO facility
CB-8	Burnt Fork Ck.	5/12/05	Dekalb	Suburban tributary to S. Peachtree Ck. in AMR
CB-9	South Peachtree Ck. @ Hahn Woods	5/12/05	Dekalb	Urbanized/Surburbanized AMR tributary to Peachtree Ck.
CB-10	North Peachtree Ck @ Druid Hills Rd.	5/12/05	Dekalb	Urbanized/Suburbanized AMR tributary to Peachtree Ck.
CB-11	Clear Ck.@Monroe Dr.	5/12/05	Fulton	Urbanized AMR stream - downstream of CSO facility
CB-12	Nancy Ck. @W. Wesley Rd.	5/12/05	Fulton	Urbanized AMR stream on main sewer line
CB-13	Peachtree Ck. @ Northside Highway	5/12/05	Fulton	Urbanized AMR stream on main sewer line
CB-14	Chattahoochee R. @ Franklin	5/13/05	Heard	Chattahoochee River downstream of AMR, terminal downstream site of study
CB-15	Acorn Ck. @ Highway 5	5/13/05	Carroll	Small rural watershed downstream of AMR
CB-16	Snake Ck. near Banning	5/13/05	Carroll	Small rural watershed downstream of AMR
CB-17	Chattahoochee R. @ Whitesburg	5/13/05	Coweta/ Carroll	Chattahoochee River downstream of AMR
CB-18	Dog River @ Highway 166	5/13/05	Douglas	Small rural watershed downstream of AMR

[1] AMR = Atlanta Metropolitan Region

Appendix 1: Description of Sampling Sites and Sample Inventory

Sample No.	Site	Sample Date	County	Description
CB-19	Chattahoochee R. @ Capps Ferry Rd.	5/13/05	Douglas/ Carroll	Chattahoochee River downstream of AMR
CB-20	Pea Ck. @ Highway 70	5/13/05	Fulton	Small rural watershed outside west of AMR
WTP-2	Utoy Ck. Water Treatment Plant	5/13/05	Fulton	Treated Sewage Effluent
CB-21	Big Ck. off S.R. 140 near	5/18/05	Fulton	Suburbanized watershed in northern AMR
CB-22	Big Ck. near Cumming	5/18/05	Forsyth	Rural/newly suburbanized watershed north of AMR
CB-23	Chestatee R. on SR 19 south of Dahlonega	5/18/05	Lumpkin	Rural watershed upstream of Lake Lanier and AMR
CB-24	Bear Ck. west of Highway 129 and east of Highway 283	5/15/05	Hall	Rural watershed upstream of Lake Lanier and AMR
CB-25	Chattahoochee R. @ State Rd. 52	5/18/05	Hall	Small rural watershed upstream of Lake Lanier and AMR
CB-26	Chattahoochee R. @ State Rd. 20	5/18/05	Gwinett/ Forsyth	Chattahoochee River immediately downstream of Lake Lanier and upstream of AMR
CB-27	Sewannee Ck. off Highway 23	5/18/05	Gwinett	Small rural/newly urbanized watershed north of AMR
CB-28	Chattahoochee R. @ State Rd. near Duluth, GA	5/19/05	Fulton/ Gwinett	Chattahoochee River immediately upstream of the AMR
CB-29	Crooked Ck. near Norcross	5/19/05	Gwinnett	Suburbanized stream in the northern AMR
CB-30	Chattahoochee R. @ Holcomb Bridge Rd.	5/19/05	Fulton/ Gwinett	Chattahoochee River in the north portion of the AMR
CB-31	Chattahoochee R. @ West Paces Ferry Rd.	5/23/05	Cobb/ Fulton	Chattahoochee River in the north portion of the AMR
CB-32	Chattahoochee R. @ State Rd. 166 west of College Park	5/23/05	Fulton/ Douglas	Chattahoochee River immediately downstream of the AMR
CB-33	Camp Ck. near Campbellton	5/23/05	Fulton	Urbanized watershed in the southern AMR
SR-1	South River @ Klondike Rd.	5/23/05	Dekalb	Ocmulgee Basin (not within the Chattahoochee River Basin) - receives treated sewage effluent from major sewage treatment plants in the AMR

Appendix 1: Description of Sampling Sites and Sample Inventory

Sample No.	Site	Sample Date	County	Description
CB-34	Sweetwater Ck. near Villa Rica	5/24/05	Douglas/ Paulding	Rural/semi-developed watershed west of the AMR
CB-35	Lick Lock Ck. @ State Rd. 92	5/24/05	Paulding	Rural/semi-developed watershed west of the AMR
CB-36	Olley Ck. north of Austell	5/24/05	Cobb	Rural/semi-developed watershed west of the AMR

Appendix 2: Chemical Analyses (in mg/L)

Sample Number	Sample Designation	Date	Temp oC	Specific Conduct. uS/cm	pH	HCO3 mg/L	Silica mg/L	Mg mg/L	K mg/L	Ca mg/L	Na mg/L	Cl mg/L	SO4 mg/L
WTP-1	RN Clayton WTP	4/14/05	NA	460.0	6.54	156.1	12	2.43	10.74	26.4	40.9	65.11	29.17
CB-1	CR near Helen	4/21/05	13.2	12.0	6.03	4.1	8	0.23	0.61	0.5	1.7	2.82	1.41
CB-2	Smith Creek	4/21/05	14.2	10.2	5.92	3.9	7	0.18	0.51	0.4	1.3	1.73	1.11
CB-3	Sweetwater Ck -1	5/9/05	18.1	70.5	6.26	32.3	15	1.83	1.33	6	6.4	8.61	3.76
CB-4	S. Utoy Creek	5/9/05	21.2	146.5	6.45	35.4	19	3.06	2.75	10.4	10.4	14.51	23.12
CB-5	N. Utoy Creek	5/9/05	19.3	131.1	6.39	46.4	18	2.36	2.47	10.9	10.0	18.19	11.83
CB-6	Utoy Creek	5/9/05	20.1	121.9	6.39	40.7	17	2.35	2.49	9.4	9.1	12.02	13.17
CB-7	Proctor Creek	5/9/05	22.9	306.5	7.10	90.3	16	5.06	4.52	30.5	19.8	28.75	41.81
CB-8	Burnt Fork Creek	5/12/05	18.0	107.9	6.50	43.1	13	2.07	2.54	10.6	7.87	12.17	4.79
CB-9	S. Peachtree Creek	5/12/05	20.0	109.5	6.56	38.2	12	2.06	2.54	10.4	5.86	13.13	5.44
CB-10	N. Peachtree Creek	5/12/05	20.5	143.9	6.52	52.5	13	2.17	2.82	15.9	11.9	17.82	7.59
CB-11	Clear Creek	5/12/05	21.5	224.3	6.66	67.1	26	3.80	4.69	19.1	16.6	27.04	27.89
CB-12	Nancy Creek	5/12/05	20.2	122.0	6.75	43.1	13	2.24	2.66	11.6	9.0	13.58	11.12
CB-13	Peachtree Creek	5/12/05	21.2	160.1	6.47	56.9	14	2.50	3.34	17.5	14.1	16.19	11.72
CB-14	CR near Franklin	5/13/05	20.3	94.2	6.69	24.4	7	1.29	2.81	6.6	10.6	15.22	8.54
CB-15	Acorn Creek	5/13/05	18.1	35.2	6.16	14.0	13	0.74	1.24	1.2	5.1	5.35	2.02
CB-16	Snake Creek	5/13/05	22.9	31.1	5.95	8.5	6	0.63	1.30	1.3	3.4	5.63	2.54
CB-17	CR at Whitesburg	5/13/05	19.5	86.2	6.21	22.8	8	1.21	1.46	5.3	9.7	14.06	6.05
CB-18	Dog River	5/13/05	20.9	46.4	6.17	12.2	11	0.85	1.51	5.1	5.3	8.16	2.11
CB-19	CR at Capps Ferry Rd	5/13/05	22.4	107.2	6.38	26.0	8	1.27	3.34	2.5	11.6	16.94	7.54
CB-20	Pea Creek	5/13/05	19.7	55.8	6.30	23.7	12	0.89	1.47	6.1	6.3	5.19	2.70
WTP-2	Utoy Creek WTP	5/13/05	NA	400.2	6.83	64.7	14	2.77	7.81	14.20	54.3	67.3	25.42
CB-21	Big Creek SR 140	5/18/05	16.6	98.9	6.36	27.7	12	2.39	3.38	6.1	8.6	21.71	4.99
CB-22	Big Creek - Cumming	5/18/05	17.2	167.9	6.15	32.5	12	5.08	5.68	6.9	17.2	49.26	9.66
CB-23	Chestatee River	5/18/05	17.2	25.6	6.00	11.3	9	0.58	0.89	1.2	2.6	7.87	1.79
CB-24	Bear Creek	5/18/05	17.2	56.1	6.09	20.0	11	1.36	2.12	2.5	4.8	6.54	1.82
CB-25	CR near Lula	5/18/05	21.6	37.1	5.77	10.7	8	0.66	1.31	1.4	3.1	4.48	1.78
CB-26	CR near Buford Dam	5/18/05	17.9	39.5	6.26	13.1	7	0.89	1.83	2.2	4.1	5.9	3.21
CB-27	Sewanee Creek	5/18/05	20.1	160.1	6.13	34.6	11	2.11	3.64	10.1	17.6	16.78	19.01
CB-28	CR near Duluth	5/19/05	13.7	46.4	6.25	16.6	5	1.00	1.95	3.2	5.0	6.93	3.95
CB-29	Crooked Creek	5/19/05	20.4	128.9	6.56	41.7	17	1.94	2.59	8.2	13.8	21.99	3.67

Sample Number	Sample Designation	Date Date	Temp oC	Specific Conduct. uS/cm	pH	HCO3 mg/L	Silica mg/L	Mg mg/L	K mg/L	Ca mg/L	Na mg/L	Cl mg/L	SO4 mg/L
CB-30	CR at Haynes Bridge Rd	5/19/05	18.9	47.5	6.41	14.0	6	0.95	2.32	2.9	4.7	6.96	3.73
CB-31	CR at W. Paces Ferry Rd	5/23/05	19.6	77.4	6.27	22.4	7	1.25	2.71	5.9	7.5	11.35	5.56
CB-32	CR at S.R. 166	5/23/05	21.5	136.3	6.73	31.5	9	1.59	3.69	9.1	19.5	21.90	10.35
CB-33	Camp Creek	5/23/05	20.3	91.0	6.41	34.3	16	1.87	2.35	6.9	7.2	8.54	4.91
SR-1	South River - Klondike Rd.	5/23/05	21.1	206.5	6.21	48.3	13	2.26	5.42	25.4	20.5	39.21	13.78
CB-34	Sweetwater Ck. - Villa Rica	5/24/05	21.1	76.7	6.57	35.0	14	2.03	1.09	5.20	5.2	4.65	2.24
CB-35	Lick Log Ck.	5/24/05	21.7	71.7	6.72	31.9	13	1.76	0.96	4.4	5.6	5.93	2.29
CB-36	Olley Ck.	5/24/05	20.7	95.2	6.48	34.6	15	1.94	2.32	8.1	6.7	12.15	4.07

Chemical Analyses (in mmol/L)

Sample Number	Sample Designation	Date	Temp oC	Specific Conduct. uS/cm	pH	HCO3 mmol/L	Silica mmol/L	Mg mmol/L	K mmol/L	Ca mmol/l	Na mmol/L	Cl mmol/L	SO4 mmol/L
WTP-1	RN Clayton WTP	4/14/05	NA	460.0	6.54	0.07	0.087	0.009	0.016	0.012	0.074	0.080	0.015
CB-1	CR near Helen	4/21/05	13.2	12.0	6.03	0.06	0.076	0.007	0.013	0.012	0.074	0.080	0.015
CB-2	Smith Creek	4/21/05	14.2	10.2	5.92	0.53	0.163	0.075	0.034	0.010	0.057	0.049	0.012
CB-3	Sweetwater Ck -1	5/9/05	18.1	70.5	6.26	0.58	0.206	0.126	0.070	0.150	0.278	0.243	0.039
CB-4	S. Utoy Creek	5/9/05	21.2	146.5	6.45	0.58	0.206	0.126	0.070	0.259	0.452	0.409	0.241
CB-5	N. Utoy Creek	5/9/05	19.3	131.1	6.39	0.76	0.195	0.097	0.063	0.272	0.435	0.513	0.123
CB-6	Utoy Creek	5/9/05	20.1	121.9	6.39	0.67	0.185	0.097	0.064	0.235	0.396	0.339	0.137
CB-7	Proctor Creek	5/9/05	22.9	306.5	7.10	1.48	0.174	0.208	0.116	0.761	0.861	0.811	0.435
CB-8	Burnt Fork Creek	5/12/05	18.0	107.9	6.50	0.71	0.141	0.085	0.065	0.264	0.342	0.343	0.050
CB-9	S. Peachtree Creek	5/12/05	20.0	109.5	6.56	0.63	0.130	0.085	0.065	0.259	0.255	0.370	0.057
CB-10	N. Peachtree Creek	5/12/05	20.5	143.9	6.52	0.86	0.141	0.089	0.072	0.397	0.518	0.503	0.079
CB-11	Clear Creek	5/12/05	21.5	224.3	6.66	1.10	0.282	0.156	0.120	0.477	0.722	0.763	0.290
CB-12	Nancy Creek	5/12/05	20.2	122.0	6.75	0.71	0.141	0.092	0.068	0.289	0.391	0.383	0.116
CB-13	Peachtree Creek	5/12/05	21.2	160.1	6.47	0.93	0.152	0.103	0.085	0.437	0.613	0.457	0.122
CB-14	CR near Franklin	5/13/05	20.3	94.2	6.69	0.40	0.076	0.053	0.072	0.165	0.461	0.429	0.089
CB-15	Acorn Creek	5/13/05	18.1	35.2	6.16	0.23	0.141	0.030	0.032	0.030	0.222	0.151	0.021
CB-16	Snake Creek	5/13/05	22.9	31.1	5.95	0.14	0.065	0.026	0.033	0.032	0.148	0.159	0.026
CB-17	CR at Whitesburg	5/13/05	19.5	86.2	6.21	0.37	0.087	0.050	0.037	0.132	0.422	0.397	0.063
CB-18	Dog River	5/13/05	20.9	46.4	6.17	0.20	0.119	0.035	0.039	0.127	0.231	0.230	0.022
CB-19	CR at Capps Ferry Rd	5/13/05	22.4	107.2	6.38	0.43	0.087	0.052	0.085	0.062	0.505	0.478	0.078
CB-20	Pea Creek	5/13/05	19.7	55.8	6.30	0.39	0.130	0.037	0.038	0.152	0.274	0.146	0.028
WTP-2	Utoy Creek WTP	5/13/05	NA	400.2	6.83	1.06	0.152	0.114	0.200	0.354	2.362	1.898	0.265
CB-21	Big Creek SR 140	5/18/05	16.6	98.9	6.36	0.45	0.130	0.098	0.086	0.152	0.374	0.612	0.052
CB-22	Big Creek - Cumming	5/18/05	17.2	167.9	6.15	0.53	0.130	0.209	0.145	0.172	0.748	1.390	0.101
CB-23	Chestatee River	5/18/05	17.2	25.6	6.00	0.19	0.098	0.024	0.023	0.030	0.113	0.222	0.019
CB-24	Bear Creek	5/18/05	17.2	56.1	6.09	0.33	0.119	0.056	0.054	0.062	0.209	0.184	0.019
CB-25	CR near Lula	5/18/05	21.6	37.1	5.77	0.18	0.087	0.027	0.034	0.035	0.135	0.126	0.019
CB-26	CR near Buford Dam	5/18/05	17.9	39.5	6.26	0.21	0.076	0.037	0.047	0.055	0.178	0.166	0.033
CB-27	Sewanee Creek	5/18/05	20.1	160.1	6.13	0.57	0.119	0.087	0.093	0.252	0.766	0.473	0.198
CB-28	CR near Duluth	5/19/05	13.7	46.4	6.25	0.27	0.054	0.041	0.050	0.080	0.217	0.195	0.041
CB-29	Crooked Creek	5/19/05	20.4	128.9	6.56	0.68	0.185	0.080	0.066	0.205	0.600	0.620	0.038

Sample Number	Sample Designation	Date	Temp oC	Specific Conduct. uS/cm	pH	HCO3 mmol/L	Silica mmol/L	Mg mmol/L	K mmol/L	Ca mmol/L	Na mmol/L	Cl mmol/L	SO4 mmol/L
CB-30	CR at Haynes Bridge RD	5/19/05	18.9	47.5	6.41	0.00	0.000	0.039	0.000	0.000	0.00	0.000	0.000
CB-31	CR at W. Paces Ferry Rd	5/23/05	19.6	77.4	6.27	0.37	0.076	0.052	0.069	0.147	0.33	0.320	0.057
CB-32	CR at S.R. 166	5/23/05	21.5	136.3	6.73	0.52	0.098	0.066	0.094	0.227	0.85	0.618	0.106
CB-33	Camp Creek	5/23/05	20.3	91.0	6.41	0.56	0.174	0.078	0.060	0.172	0.31	0.241	0.050
SR-1	South River - Klondike Rd.	5/23/05	21.1	206.5	6.21	0.79	0.141	0.094	0.139	0.634	0.89	1.106	0.141
CB-34	Sweetwater Ck. - Villa Rica	5/24/05	21.1	76.7	6.57	0.57	0.152	0.084	0.028	0.130	0.23	0.131	0.023
CB-35	Lick Log Ck.	5/24/05	21.7	71.7	6.72	0.52	0.141	0.073	0.025	0.110	0.24	0.167	0.023
CB-36	Olley Ck.	5/24/05	20.7	95.2	6.48	0.57	0.163	0.080	0.059	0.202	0.29	0.343	0.042

Chemical Analyses (in meq/L)

Sample Number	Sample Designation	Date	Mg meq/L	K meq/L	Ca meq/L	Na meq/L	Sum Equiv. Cations meq/L	Cl meq/L	SO4 meq/L	HCO3 meq/L	Sum Equiv. Anions meq/L	Charge Balance %
WTP-1	RN Clayton WTP	4/14/05	0.200	0.275	1.317	1.779	**3.571**	1.837	0.304	2.56	**4.699**	-13.6
CB-1	CR near Helen	4/21/05	0.019	0.016	0.025	0.074	**0.133**	0.080	0.015	0.07	**0.161**	-9.5
CB-2	Smith Creek	4/21/05	0.015	0.013	0.020	0.057	**0.104**	0.049	0.012	0.06	**0.124**	-8.7
CB-3	Sweetwater Ck -1	5/9/05	0.151	0.034	0.299	0.278	**0.762**	0.243	0.039	0.53	**0.812**	-3.1
CB-4	S. Utoy Creek	5/9/05	0.252	0.070	0.519	0.452	**1.293**	0.409	0.241	0.58	**1.230**	2.5
CB-5	N. Utoy Creek	5/9/05	0.194	0.063	0.544	0.435	**1.236**	0.513	0.123	0.76	**1.397**	-6.1
CB-6	Utoy Creek	5/9/05	0.193	0.064	0.469	0.396	**1.122**	0.339	0.137	0.67	**1.143**	-0.9
CB-7	Proctor Creek	5/9/05	0.416	0.116	1.522	0.861	**2.915**	0.811	0.435	1.48	**2.727**	3.3
CB-8	Burnt Fork Creek	5/12/05	0.170	0.065	0.529	0.342	**1.107**	0.343	0.050	0.71	**1.100**	0.3
CB-9	S. Peachtree Creek	5/12/05	0.169	0.065	0.519	0.255	**1.008**	0.370	0.057	0.63	**1.053**	-2.2
CB-10	N. Peachtree Creek	5/12/05	0.179	0.072	0.793	0.518	**1.562**	0.503	0.079	0.86	**1.442**	4.0
CB-11	Clear Creek	5/12/05	0.313	0.120	0.953	0.722	**2.108**	0.763	0.290	1.10	**2.153**	-1.1
CB-12	Nancy Creek	5/12/05	0.184	0.068	0.579	0.391	**1.223**	0.383	0.116	0.71	**1.205**	0.7
CB-13	Peachtree Creek	5/12/05	0.206	0.085	0.873	0.613	**1.778**	0.457	0.122	0.93	**1.511**	8.1
CB-14	CR near Franklin	5/13/05	0.106	0.072	0.329	0.461	**0.968**	0.429	0.089	0.40	**0.918**	2.7
CB-15	Acorn Creek	5/13/05	0.061	0.032	0.060	0.222	**0.374**	0.151	0.021	0.23	**0.401**	-3.5
CB-16	Snake Creek	5/13/05	0.052	0.033	0.065	0.148	**0.298**	0.159	0.026	0.14	**0.325**	-4.3
CB-17	CR at Whitesburg	5/13/05	0.100	0.037	0.264	0.422	**0.823**	0.397	0.063	0.37	**0.833**	-0.6
CB-18	Dog River	5/13/05	0.070	0.039	0.254	0.231	**0.594**	0.230	0.022	0.20	**0.452**	13.5
CB-19	CR at Capps Ferry Rd	5/13/05	0.104	0.085	0.125	0.505	**0.819**	0.478	0.078	0.43	**0.983**	-9.1
CB-20	Pea Creek	5/13/05	0.073	0.038	0.304	0.274	**0.689**	0.146	0.028	0.39	**0.563**	10.1
WTP-2	Utoy Creek WTP	5/13/05	0.228	0.200	0.709	2.362	**3.498**	1.898	0.265	1.06	**3.224**	4.1
CB-21	Big Creek SR 140	5/18/05	0.197	0.086	0.304	0.374	**0.962**	0.612	0.052	0.45	**1.118**	-7.5
CB-22	Big Creek - Cumming	5/18/05	0.418	0.145	0.344	0.748	**1.656**	1.390	0.101	0.53	**2.023**	-10.0
CB-23	Chestatee River	5/18/05	0.048	0.023	0.060	0.113	**0.243**	0.222	0.019	0.19	**0.426**	-27.3
CB-24	Bear Creek	5/18/05	0.112	0.054	0.125	0.209	**0.500**	0.184	0.019	0.33	**0.531**	-3.1
CB-25	CR near Lula	5/18/05	0.054	0.034	0.070	0.135	**0.293**	0.126	0.019	0.18	**0.320**	-4.5
CB-26	CR near Buford Dam	5/18/05	0.073	0.047	0.110	0.178	**0.408**	0.166	0.033	0.21	**0.415**	-0.8
CB-27	Sewanee Creek	5/18/05	0.174	0.093	0.504	0.766	**1.536**	0.473	0.198	0.57	**1.238**	10.7
CB-28	CR near Duluth	5/19/05	0.082	0.050	0.160	0.217	**0.509**	0.195	0.041	0.27	**0.509**	0.1
CB-29	Crooked Creek	5/19/05	0.160	0.066	0.409	0.600	**1.235**	0.620	0.038	0.68	**1.342**	-4.1

Sample Number	Sample Designation	Date	Mg meq/L	K meq/L	Ca meq/L	Na meq/L	Sum Equiv. Cations meq/L	Cl meq/L	SO4 meq/L	HCO3 meq/L	Sum Equiv. Cations meq/L	Charge Balance %
CB-30	CR at Haynes Br.Rd.	5/19/05	0.079	0.059	0.145	0.20	**0.487**	0.196	0.076	0.23	**0.502**	-1.5
CB-31	CR at W. Paces Ferry Rd	5/23/05	**0.104**	0.069	0.294	0.33	**0.794**	0.320	0.113	0.37	**0.801**	-0.5
CB-32	CR at S.R.166	5/23/05	0.132	0.094	0.454	0.85	**1.529**	0.618	0.211	0.52	**1.345**	6.4
CB-33	Camp Creek	5/23/05	0.155	0.060	0.344	0.31	**0.873**	0.241	0.100	0.56	**0.903**	-1.7
SR-1	South River-Klondike Rd.	5/24/05	0.187	0.139	1.267	0.89	**2.485**	1.106	0.281	0.79	**2.179**	6.6
CB-34	Sweetwater Ck. -Villa Rica	5/24/05	0.168	0.028	0.259	0.23	**0.682**	0.131	0.046	0.57	**0.751**	-4.8
CB-35	Lick Log Ck.	5/24/05	0.146	0.025	0.220	0.24	**0.634**	0.167	0.047	0.52	**0.737**	-7.5
CB-36	Olley Ck.	5/24/05	0.161	0.059	0.404	0.40	**0.916**	0.343	0.083	0.57	**0.993**	-4.0
											Average	**4.8%**