

Report for 2003GA40B: "A Combined Hydrological , Geochemical and Isotopic Approach to Understanding the Effects of Basin Scale on Base Flow Systematics in the Georgia Piedmont"

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Report Follows

**A Combined Hydrological, Geochemical and Isotopic
Approach to Understanding the Effects of Basin Scale
on Base Flow Systematics in the
Georgia Piedmont Province**

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for the:**

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ABSTRACT

The major ion geochemistry and isotopic (^3H concentrations, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) variability was investigated for the period between March, 2003 and March, 2004 in the Middle Oconee River basin near Arcade, Georgia. Tritium concentrations were higher in base flow and shallow ground water than in recent rainfall indicating that the ground water is stored within these Piedmont Province watersheds for several decades prior to its release as base flow. The lack of appreciable $\delta^{18}\text{O}$ variability indicates that there is not a significant component of seasonal rainfall within stream base flow and therefore the increased rate of base flow that occurs during the cooler winter and early spring months in Piedmont stream basins can not be directly related to seasonal influx. There was some geochemical variation within base flow in all four stream basins; however F-tests indicate that the greatest variability was associated with the 3.9 km² Indian Creek watershed which was the smallest of the basins analyzed and most subjected to contaminant input. The major ion geochemistry (e.g. alkalinity and magnesium ion concentrations) of base flow did not vary strictly as a function of basin scale or seasonal water fluctuations; however, mass balance models that assume the chemical composition of base flow is constant on a year-round basis are not correct.

The strontium isotopic data collected for this study likely represents the first of its kind for this region. Strontium isotope ratios were virtually temporally invariant at a given stream location and each stream basin was characterized by its unique range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increased with basin scale although strontium ion concentration varied over a similar range in all base flow. The unique $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is likely the best parameter that can be used

in future studies involving mixing processes in Piedmont Province watersheds, aquifers, lakes, and reservoirs.

PROJECT DESCRIPTION

Introduction and Overview:

One of the critical areas emerging in hydrological science that has been identified by the National Research Council (National Academy of Science, 1991) involves improvement in our understanding of how spatial and temporal scales are linked in converting rainfall to runoff (Hornberger and Boyer, 1995). Most studies of the hydrological, hydrochemical and isotopic dynamics of watersheds are done on a small scale (i.e. watershed area $< 1.0 \text{ km}^2$) and emphasize the dynamics of storm flow. Integrating the dynamics of small watersheds to larger drainage networks is rarely undertaken and therefore it is not clear whether results gleaned from small upstream watersheds apply to the larger downstream basins that are often used for surface water resources by municipalities. In one of the few studies which considered spatial scales, Turner and Macphersen (1990) concluded that the processing of stable isotopes and major ions within a rural Western Australia catchment were very different on the 1 to 30 km^2 scale. It is implicit that understanding the spatial scale effects upon major ion and isotopic processing will also lead to a better understanding of the meaning of temporal variations within watersheds.

During most years base flow provides a perennial source of stream flow and is the dominant water resource for municipalities located within the Piedmont Province of Georgia (see information that follows in this report). A significant shortcoming of the present state of hydrological science is that base flow variation (both seasonal and spatial) has not been given sufficient attention in that most previous watershed studies have intensively focused upon storm

period dynamics. This limitation is unfortunate in that ground water sustains a year-round water resource in humid regions and provides a significant component to the storm hydrograph (see references in the literature review). Furthermore, in many hydrological settings such as the Piedmont Province, yearly base flow rates vary widely (e.g. by a factor of 3-5) which strongly suggests that multiple mechanisms and/or source areas are involved in sustaining stream flow on a year-round basis. A better understanding of base flow generation and the associated variability with respect to flow rates can be derived using isotopic and geochemical tracers. The environmental isotopic investigation of base flow was initiated in the Georgia Piedmont by the Principal Investigator a decade ago (Rose, 1993 and Rose, 1996). However, much more work needs to be done in this area, particularly in terms of relating base flow geochemical and isotopic variation to basin scale.

This study investigated the isotopic and geochemical variation of base flow within a Piedmont basin (the Middle Oconee River, near Arcade, GA which is 35 km northeast of the Atlanta metropolitan region and 10 km north of Athens, GA) on spatial scales that range between 1.0 and 1,000 km². The spatial and temporal investigation of the isotopic variability of base flow (along with rainfall and ground water) has led to a better understanding of how variable source areas contribute to stream flow in the Piedmont setting and perhaps elsewhere.

Objectives:

Broader Hydrological Objectives: The primary objectives of this investigation were as follows:

1) To investigate the scale at which the major ion geochemistry and isotopic ($\delta^{18}\text{O}$, strontium isotope ratios, and environmental tritium) homogenization processes affect the

composition of base flow in an integrated drainage basin. This is an important question that has not been systematically addressed within the hydrological sciences to date.

2) To develop a better understanding of how the isotopic and geochemical characteristics and variability of base flow compare to that of ground water within a drainage basin. [Base flow in this report is defined as stream flow that appears on a hydrograph following storm recessions and before storm events which mostly consists of ground water discharge; after Pionke et al., 1988].

3) To investigate how the combined use of strontium and stable oxygen isotope ratios, environmental tritium, and major ion geochemistry might collectively be used to identify variable source areas, mixing processes, and residence times which control the hydrodynamic and hydrochemical dynamics of base flow in the southeastern Piedmont Province.

4) To develop a better understanding of how strontium isotope systematics can be used with the meteoric isotopes (stable oxygen ratios and tritium) in watershed science.

5) To broaden our understanding of how the isotopic study of watershed dynamics conducted on small drainage basins (i.e. $\leq 1-10 \text{ km}^2$) relate to those of larger, more integrated basins on the scale of several hundred square kilometers.

The above-stated objectives are all interrelated in that base flow might be regarded as a mixture of ground water (and possibly vadose zone water) derived from various sources within a watershed. These sources include ground water from the near-stream zone as well as from more distal portions of the watershed. An understanding of these isotope systematics will in turn lead to a better understanding of how the variable source areas within a watershed contribute to stream flow between storm periods under a range of hydrological conditions.

Objectives Specific to the Study Area:

1) To better define the seasonal variability of environmental isotopes (i.e. tritium, stable oxygen isotopes, strontium-87/strontium-86) in rainfall, base flow and ground water and how this variation relates to sources of water in Piedmont Province watersheds. To my knowledge, strontium isotope ratios have not yet been used within this hydrological setting and it is therefore possible that the proposed research can break new ground in this area.

2) To integrate the results of this study with previous related studies in the Piedmont Province (e.g Rose, 1993; Rose, 1996; and Wenner et al., 1991) in order to better define regional isotopic trends and their possible hydrological significance.

3) To investigate the effects of scale upon base flow generation within Piedmont Province watersheds.

4) To determine whether the increased base flow rates that occur in the late winter and early spring in Piedmont watersheds are the result of the contribution of new, seasonally-derived water or some other mechanism.

5) To facilitate the rational development of a Piedmont Province watershed by providing an in-depth analysis while the study basin is in a relatively undeveloped state. The proposed Middle Oconee River study basin is juxtaposed in between three growth regions - Gainesville, GA; Athens, GA; and the eastern Atlanta metropolitan region - and will likely become a prime site for future residential development.

BACKGROUND AND LITERATURE REVIEW

The following section presents a summary of some of the major research directions that have occurred in watershed science during the past several decades. These topics are presented

in terms of how they are relevant to the research described herein and no attempt is made in the limited space available to exhaustively cover these topics on their own merits.

Hydrograph Separation:

The detailed utilization of environmental isotopic tracers for water sources within watersheds has primarily focused upon the stable isotopes of oxygen and hydrogen within storm runoff. These studies have most often been undertaken in watersheds with areas that are less than 10 km² (Table 10.1 in Genereux and Hooper, 1998). Such an approach has unquestionably advanced our knowledge of watershed dynamics by allowing the careful comparison of inputs (rainfall and snow melt) and outputs (stream flow). The primary focus of most watershed studies that have used isotope and geochemical systematics has been upon hydrograph separation which assesses the relative contribution of ground water, soil water, and direct surface water runoff to total storm runoff.

Two of the key assumptions that are inherent within the geochemical and isotopic hydrograph separation method are that the ground water or pre-event component is geochemically distinct from the event water and that both the pre-event and event components remain geochemically or isotopically constant during the course of the storm and after (Sklash and Farvolden, 1979). If the vadose zone contribution is isotopically or geochemically distinct from that of the ground water, the storm hydrograph can be separated into three components (Dewalle et al., 1988). The major conclusion drawn from these studies is that old or pre-event water comprises a significant (i.e. 20-60%) proportion of the total storm flow. However, chemical and isotopic methods of hydrograph separation are hampered by the

lack of knowledge regarding both the temporal and spatial isotopic and geochemical variability of those sources contributing to storm flow (Kendall, 2001).

End-Member Mixing Models:

An often-used method of analyzing possible source area contributions to stream flow involves end-member mixing analysis (Christopherson et al., 1990; Hooper et al., 1990; Katsuyama et al., 2001; and Burns et al., 2001). This involves graphical analysis in which two chemical and/or isotopic parameters are used to represent the designated end members (often these are throughfall, vadose zone ground water or interflow, and saturated zone ground water; Katsuyama et al., 2001). Such a method is very useful in demonstrating that mixing has occurred; however, the *a priori* designation of end members along with their chemical and isotopic composition can be problematic (e.g. different sets of end members have been used to model the stream water chemistry for the same small Panola Mountain catchment in the Georgia Piedmont; Hooper et al., 1990 and Burns et al., 2001). Furthermore, these models are based upon the assumed chemical and/or isotopic constancy of the components involved in the mixing process (Hooper et al., 1990). The assumption of constancy has been questioned by numerous investigators in that the chemical composition of all components including ground water can change during and after a storm (Anderson et al., 1997 and Kendall et al., 2001).

It is possible that base flow itself represents a seasonally changing mixture of different end members from various source areas which include but are not necessarily limited to the riparian saturated zone, the riparian vadose zone, and the hillslope saturated zone. The simple graphical procedures which have been developed to analyze the components of storm water can be used to analyze possible *components* of the base flow mixture. If the end-member compositions are not known with great confidence, such plots could still reveal whether water

samples fall within a mixing triangle which is indicative of three end-member mixing), on a mixing line (two end-member mixing) or cluster around a point, suggesting stream flow evolves from one more-or-less temporally invariant source.

Seasonal Variation of Stream Water Chemistry and Isotopic Composition:

The variation of solute chemistry and isotopic composition of stream water has been shown to vary on many drainage basin scales (e.g. Piñol et al, 1992; Taylor and Hamilton, 1993 and DeWalle et al., 1997). One of the major factors responsible for this variation include the contribution of variable proportions of ground water with its characteristically longer residence times. This usually results in increased solute concentrations (Ohrui and Mitchell, 1999) and less isotopic variability. Other factors include the seasonal variation of the isotopic composition of rainfall, changes in the water balance related to seasonal evapotranspiration rates, and the diminished contribution of chemically dilute vadose zone water during the dry season.

Rose (1995 and 1996) found the $\delta^{18}\text{O}$ composition of both base flow and ground water within the southern Georgia Piedmont regolith to be variable and not equivalent to one another. Fredericksen and Criss (1999) derived similar findings in their study of a karstic watershed in eastern Missouri. Rose (1994) found that base flow alkalinity and base cation concentrations showed systematic temporal variation within the Falling Creek basin (southern Georgia Piedmont) as a result of the influx of additional water that occurs during the late autumn to early spring. However, Wenner et al. (1991) concluded that the $\delta^{18}\text{O}$ variations are substantially dampened at rather shallow depths and that $\delta^{18}\text{O}$ composition of base flow in a small Georgia Piedmont watershed is virtually time-invariant. Therefore, more comprehensive and exhaustive

studies are required to define the range of seasonal isotopic variation within shallow ground water and base flow and to discern its hydrological significance within the Piedmont setting.

Mechanisms for Base Flow Generation and Possible Causes of Spatial and Temporal

Isotopic Variation in Stream Base Flow:

Ground-water discharge has long been cited as the dominant mechanism responsible for the generation of base flow, or that water which sustains stream flow between storm events (Freeze, 1974). The literature is not replete with discussion regarding the systematics of isotopic or geochemical variation within base flow; however, McDonnell et al. (1991) showed that stable hydrogen isotope ratios in the ground water contribution to stream flow varied in a spatially systematic manner along hillslopes within a small, steep New Zealand watershed. Gat (1974) showed that the stable isotopic ($\delta^{18}\text{O}$) composition of ground water in an Israeli coastal aquifer is greater than analytical error and that ground water within a mountain aquifer displayed a wide range of spatial and temporal isotopic variability.

In their mathematical analysis of base flow generation, Ophori and Tóth (1990) concluded that the contribution of base flow to total stream flow increases with basin area. Furthermore, their stream line analyses indicate that ground water which evolves from a specific recharge area can bypass local tributaries and eventually discharge into a higher order stream (Figure 6, Ophori and Tóth, 1990). Harris et al. (1995), on the basis of isotopic analysis, divided saturated zone contributions to stream flow into two distinct sources: a near-stream reservoir which mixes with direct precipitation and an upslope reservoir which does not mix with another water source. These analyses are consistent with the variable source area concept and imply that there are many flow paths to streams which differentially process the isotopic variation inherent within rainfall or recharge. Hewlett and Nutter (1970) developed the concept of the areally

expanding watershed for storm runoff and it is possible that those source areas which contribute to base flow also seasonally expand and contract. Very little attention has been paid to the spatial variability of pre-event water (i.e. that water which makes up base flow and ground water) over a suitably wide range of watershed scales (Genereux and Hooper, 1998) and therefore our knowledge of variable source area contributions to >pre-event water= or base flow is limited.

If we can assume that base flow is generated from variable source areas within a watershed that are at least partially characterized by transient conditions (Hewlett and Hibbert, 1963), it is likely that both the isotopic and geochemical composition vary co-systematically with these transient conditions. Furthermore, it is possible that the >inverse method= can be invoked and the seasonal and spatial variability of base flow along with the relative degree of isotopic homogenization can be utilized to identify possible source areas and the mechanisms that are responsible for its generation.

Residence Times:

Quantification of the mean residence times of ground water, soil water, and base flow can lead to a better understanding of the origins of stream flow and mixing processes that occur within watersheds. Most studies of this type (e.g. McGuire et al., 2002 and Stewart and McDonnell, 1991) rely upon seasonal differences with respect to the $\delta^{18}\text{O}$ or δD inputs (precipitation) contrasted with the stable isotope output (stream flow) for the analysis of residence time. Similar studies have also utilized environmental tritium inputs and outputs (e.g. Maloszewski et al., 1992). Mathematical models typically involve the utilization of the >convolution integral= and rely upon *a priori* assumptions regarding the nature of ground-water flow through a basin (i.e. whether it is >piston=, >dispersive= or some other type of flow)

[Maloszewski and Zuber, 1992]. Frederickson and Criss (1999), using a >damped average= model of $\delta^{18}\text{O}$ values, showed that there is a large discrepancy between the modeled residence times between river water and spring water in the Meramec River Basin in eastern Missouri.

Rose (1993,1995, and 1996) has shown through a model based upon decay-corrected tritium input concentrations that the mean residence time of base flow and ground water in the Georgia Piedmont is ~15-40 years. Burns et al. (2003) recently concluded on the basis of tritium-helium and chlorofluorocarbon dating that deeper ground water within the riparian zone of the Panola Mountain research watershed was 26-27 years old. Furthermore, Burns et al. (2003) concluded that stream flow becomes progressively older downstream. The relationship between the mean residence time of base flow, ground water and spatial scale within Piedmont watersheds has not been systematically addressed as of yet. One important question related to residence times that has not been answered is whether the additional base flow that occurs within Piedmont basins during the late winter and spring is comprised of >new=, seasonally-derived water.

Strontium Isotopes:

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio analyses have been utilized only to a limited extent in catchment hydrology and to my knowledge there have not been previous studies that have incorporated strontium isotope systematics within Piedmont Province watersheds. Strontium isotope ratios or *signatures* are derived from mineral-water interactions, rather than from the atmosphere (Ninz, 1998). Hence, they serve as perfect complementary information to stable oxygen ratios ($\delta^{18}\text{O}$ and δD) and tritium which are atmospherically derived tracers. Strontium-87 is produced from the beta decay of rubidium-87; therefore, alkali-rich minerals such as mica commonly produce higher or

more *radiogenic* $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than other non-radiogenic minerals such as calcite. Typically, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are used to identify ground water flow paths and mixing ratios in aquifers (e.g. Musgrove and Banner, 1993 and Lyons et al., 1995). Wadleigh et al. (1995) used strontium isotope ratios to assess the contribution of different watershed areas to stream flow and stream water chemistry. The mixing of water bodies from various sources can be discerned by plotting $^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus strontium ion concentrations (Faure, 1986).

There are numerous other controls upon $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in addition to source minerals that when properly interpreted can lead to a better understanding of the hydrodynamics of watersheds and aquifers. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of rainwater compositions is usually much different than that of a solution derived from mineral weathering and therefore the isotopic composition might indicate the relative contribution of recent precipitation to natural water (Bailey, 1996; Hogan et al., 2000 and Douglas et al., 2002). There is often a strong correlation between the rates 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 and other mixing processes that also control the isotopic composition of strontium (Négrel and Lachassagne, 2000).

Biotite is the most radiogenic of the common aluminosilicate minerals in that rubidium is a common substitute for potassium (Bullen and Kendall, 1988) and other radiogenic sources include K-feldspar, garnet and hornblende (Bailey et al., 1996). Strontium isotopic ratios within natural waters typically better reflect the ratio of individual minerals rather than whole rock ratios because of different weathering rates (Aubert et al., 2002). The degree of weathering is

one factor that controls strontium isotope ratios; however, other less cited but potentially important controls include discharge rates (Aubert et al., 2002) and the degree to which Sr^{+2} is absorbed upon clay soils (Katz and Bullen, 1996). The age of minerals is another control upon the $^{87}\text{Sr}/^{86}\text{Sr}$ 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).

Nakano et al. (2001) reported that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within soil water in central Japan were highly variable (partially as the result of ion exchange) while the ratios in base flow were nearly constant. These studies suggest that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can potentially be used to trace water emanating from the vadose zone as opposed from deeper (more isotopically homogenized) ground-water flow paths. The co-systematic interpretation of strontium isotope ratios and Sr ion concentrations with major ion geochemical parameters, stable oxygen isotope ratios, and environmental tritium offers a potentially powerful means of identifying and quantifying contributions from variable source areas (e.g. near-stream zone versus longer and deeper ground water flow paths) to stream flow in the Piedmont Province and elsewhere.

STUDY AREA

Land Use and Geology:

The 860 km² Middle Oconee River basin study area (Figure 1) in northeastern Georgia was chosen for this study in that it is relatively undeveloped and can be readily accessed for monthly sampling from Atlanta. The basin which is predominantly within Jackson County, Georgia is comprised of ~95% forest and pasture land (determined on the basis of the digital images in Alhadeff, 2001) and only a few small municipalities that include Pendergrass, Jefferson, and Braselton are located within its boundaries. However the basin is far from pristine

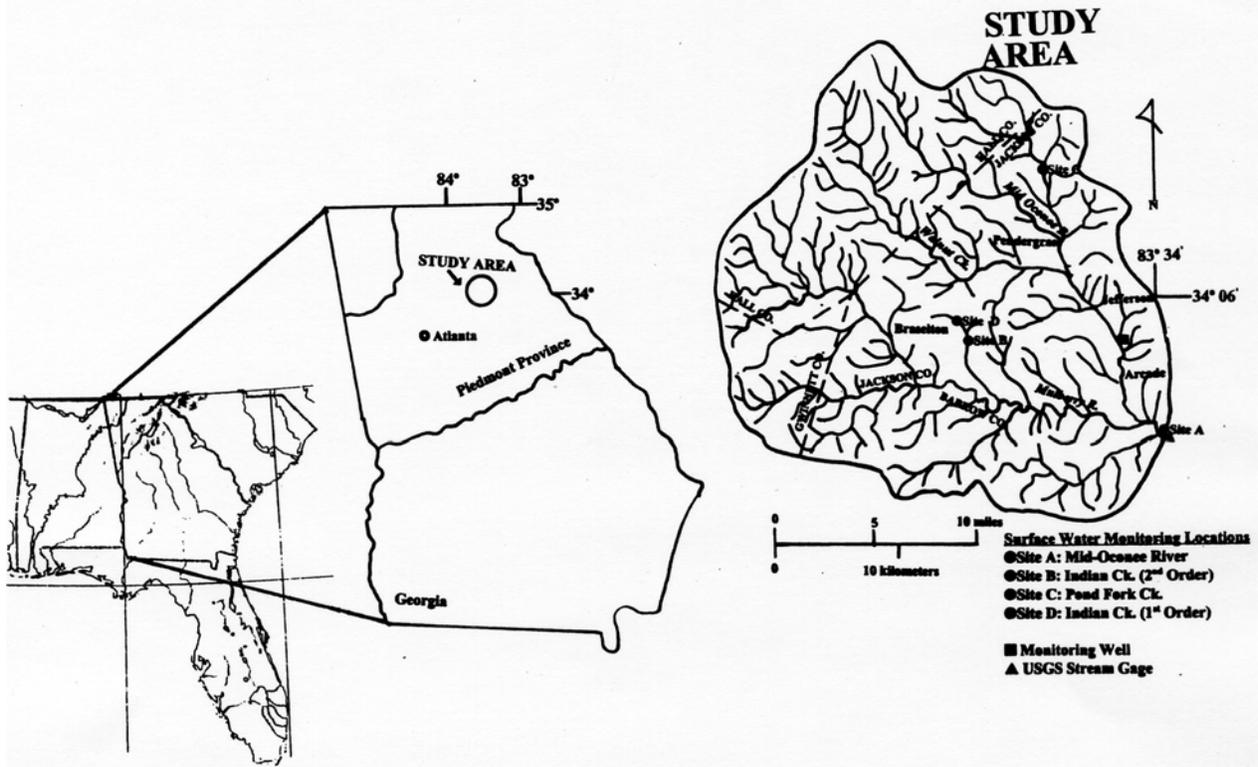


Figure 1. Map of the study area showing sampling locations

in that the Middle Oconee River currently receives effluent from a few relatively low-capacity sewage treatment plants and numerous septic tanks are present throughout the basin. Historically, the basin has been used for agricultural activities, leaving hundreds of acres of clear-cut land.

As is typical of the Georgia Piedmont, the Middle Oconee River study basin is underlain by Paleozoic metamorphic rocks that are dominantly biotite gneiss, mica schist and amphibolite schists (Figure 2). Thick columns of well-weathered, dark brown silty-clay soils (dominantly ultisols) overly the bedrock in most locations. The basin is well-incised with a complex network of streams that range from first to fifth order (Figure 1). The bedrock in this region is mantled by

0-50 meters of regolith with an average thickness of 20 meters (LeGrand, 1967). The regolith consists predominantly of ultisols (sandy clay soils with abundant iron oxyhydroxides), saprolites and alluvium near stream channels (Heath, 1964). Slopes within the Middle Oconee River basin are gradual (generally < 4%) which is typical of the Piedmont Province region as a whole. Stream flow within forested regions in the Georgia Piedmont has been approximated as a mixture of water stored from a shallow organic horizon, hill-slope ground water and deeper ground water within the soil mantle (Hooper et al., 1990). Deeper hillslope ground water stored near the bedrock surface - soil contact has been shown to be an important water source to streams in this setting (McDonnell et al., 1996).

Four stream locations (Indian Creek - first order tributary, Indian Creek - second order tributary, Pond Fork Creek, and the Middle Oconee River near Arcade, Georgia) were chosen as sampling sites in that they represent watershed areas between 3.9 - 860 km² (Figure 1 and Table 1). Of the four stream basins, Pond Fork Creek (watershed area = 54 km²) in the northwestern portion of the study area is the least developed. The Middle Oconee River (watershed area = 860 m²) which is the terminal basin of the study area is the only stream directly impacted by water treatment plant effluent. The small first-order Indian Creek watershed (watershed area = 3.9 km²) is used as a horse pasture and is therefore the stream that is most significantly impacted by potential contamination from land use practices.

**Table 1
Description of Sampling Sites**

	Middle Oconee River near Arcade, Ga¹	Pond Fork Creek	Indian Creek (1st order)	Indian Creek (2nd order)	Shallow Ground Water Monitoring Well^{2,3}	Rainfall Collection Site
Latitude	34° 01'	34° 12'	34° 05'	34° 05'	34° 05'	33° 49'
Longitude	83° 34'	83° 40'	83° 44'	83° 44'	83° 35'	84° 16'
County	Jackson	Jackson	Jackson	Jackson	Jackson	Dekalb
Watershed Area (km²)	860	54	3.9	12.7	-----	-----
Elevation (masl)⁴	210	235	270	255	240	-----
Bedrock Lithology	biotite gneiss mica schist amphibolite schist amphibolite	biotite gneiss mica schist amphibolite	Amphibolite Schist	Amphibolite Schist	biotite gneiss mica schist amphibolite	-----

¹USGS gage site: 022174745;

²Well Depth = 17 meters, average water table depth = 8.4 meters below land surface;

³well completed in dark red brown sandy, silty, clay soils

⁴meters above mean sea level

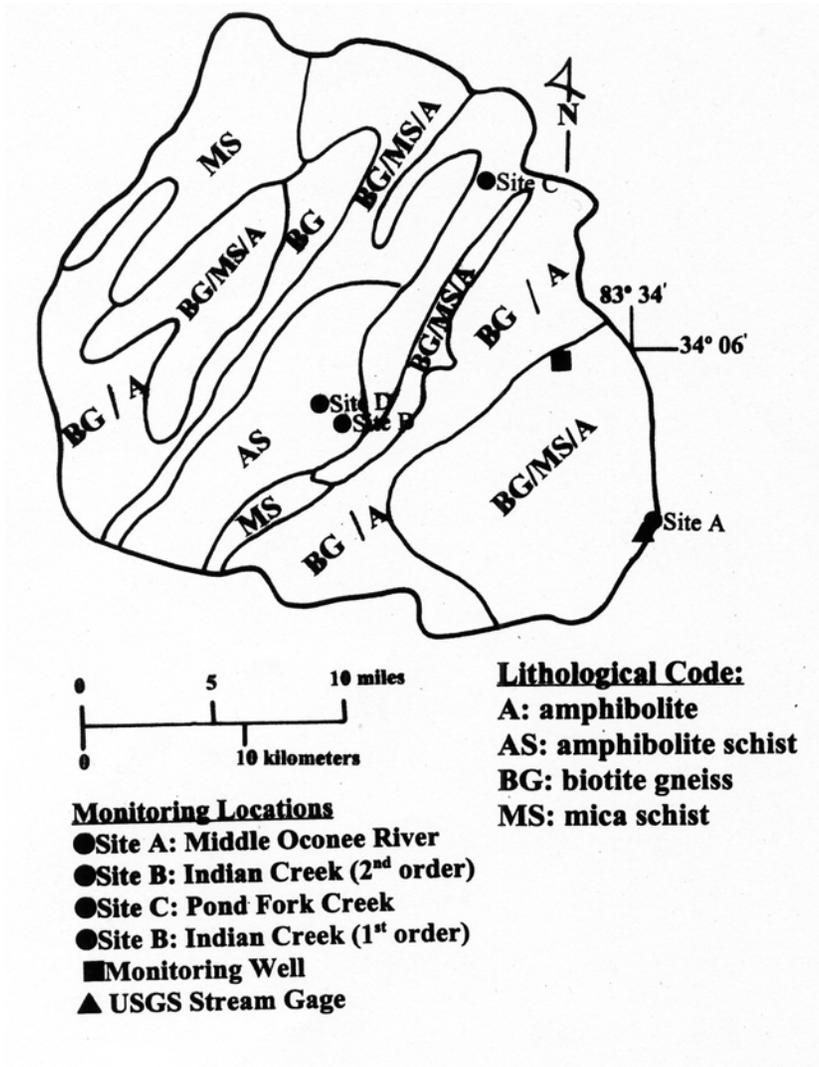


Figure 2. Geological map of the study area (after Alhadeff et al., 2001)

Hydrology:

The study area receives an average annual rainfall total of 1215 millimeters (mm) as determined from a U.S. Department of Agriculture gaging site located 15 km south of the basin (see Methods section). The average runoff for the Middle Oconee basin for the period of record between 1987 - 2002 was 438 mm or 36% of total precipitation. The average annual rate of base flow during this period as determined from hydrographic analysis is estimated to be 226 mm or 50% of total stream flow. This estimate of base flow interestingly is almost identical to the rate of *effective recharge* which was independently calculated for the Blue Ridge and Piedmont Provinces in Virginia (Nelms et al., 1997). Base flow rates within the study basin and in the region vary greatly and during wet years base flow provides 40% of the total stream flow and during dry years 70-80%.

Stream runoff and base flow in the study area are seasonal with the highest rates occurring during the Winter and Spring months when evapotranspiration rates are the lowest. The seasonal water balance for the Watkinsville, Georgia atmospheric monitoring site (10km southeast of the study basin) is shown on Figure 3 and it is clear that a potential water deficit (potential evaporation rates > precipitation rates) exists during the period between May through September (data from the Georgia Automated Environmental Monitoring Network, 2004). Average monthly low flow rates (an approximation of base flow) for the Middle Oconee River

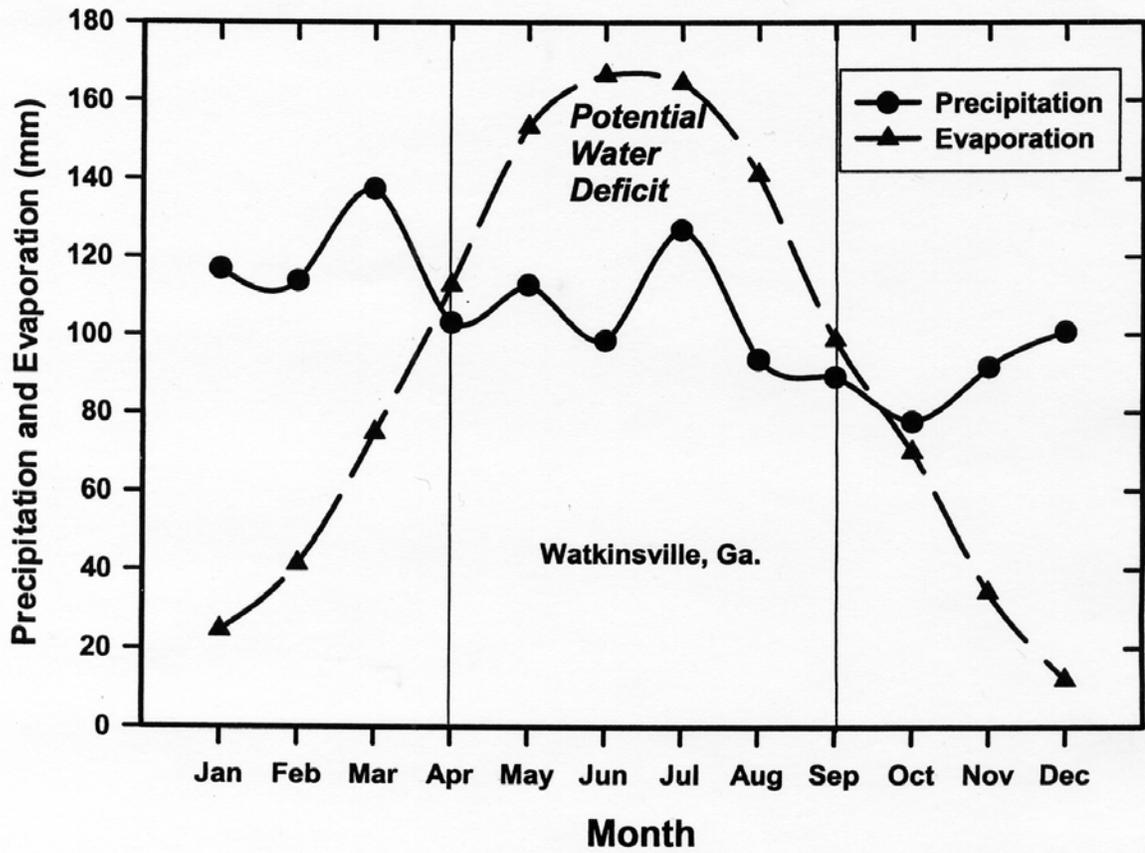


Figure 3. Monthly water budget for the study area

reach their minimum value of 10 mm during September and October and their maximum value of 28 mm in March. This approximate three-fold increase in the rate of base flow is very typical of the hydrodynamics of most streams in the Georgia Piedmont Province (Figure 4; data from U.S. Geological Survey, 2004a). The most important aspect of base flow is perhaps not the absolute magnitude; rather it is the estimated 75-90% of the year in which it provides the sole surface water resource. In short, base flow is the dominant water resource of the region (Rose, unpublished data).

METHODS

Data Collection, Field Methods and Sampling Methods:

Time-series samples of rainfall, shallow ground water, and stream base flow were typically collected on a monthly basis during the period between March, 2003 and March, 2004. In order to facilitate storm-by-storm collection and to minimize evaporation effects, rainfall was collected at the principal investigator's residence in Decatur, Georgia 50 km east of Middle Oconee River watershed. Rainfall was collected in polyethylene sampling bottle attached to a funnel. Rainfall was gaged at the site in order to weight the precipitation samples by the amount of rainfall collected. The rainfall samples were thought to be collected sufficiently close to the study area as to be representative of conditions within the watershed. Daily precipitation values were obtained from the Georgia Automated Environmental Network (2004) for the U.S. Department of Agriculture weather station located 10 km south of the study basin at Watkinsville, Georgia.

Stream discharge values were obtained on a daily basis from a U.S. Geological Survey automated stream gage emplaced on the Middle Oconee River near Arcade, Georgia (U.S.

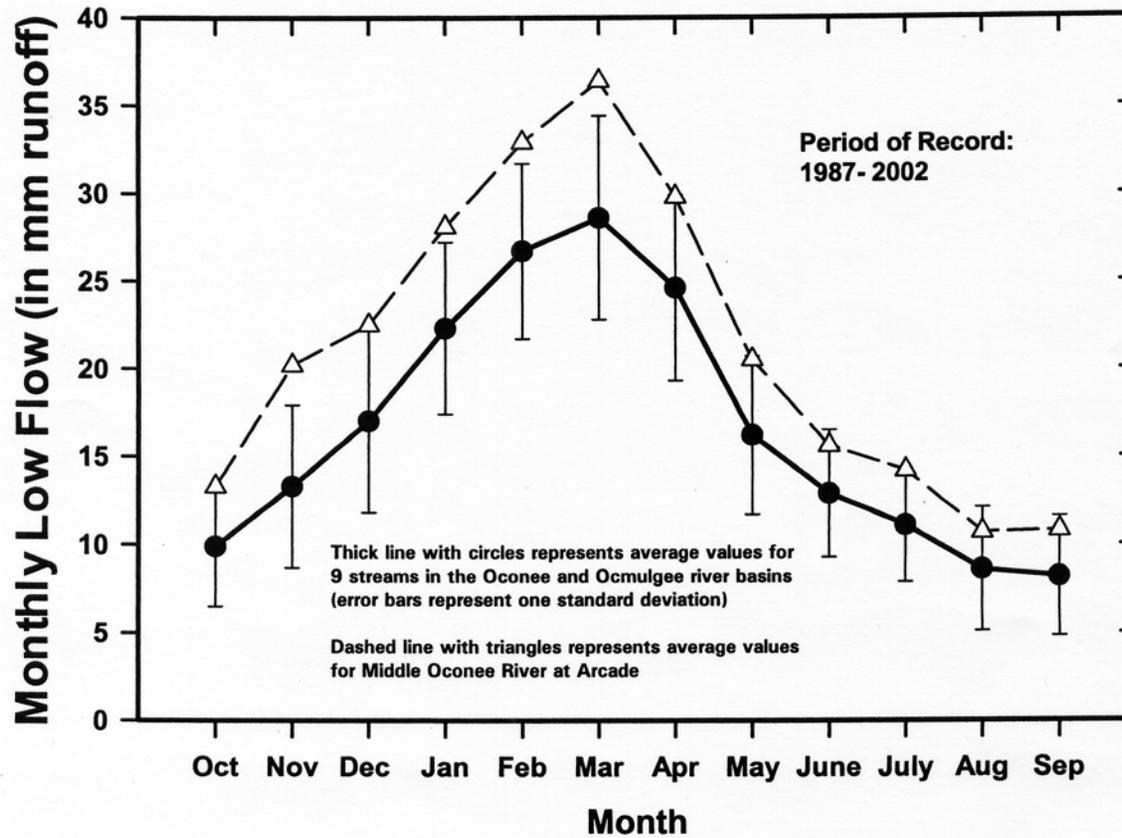


Figure 4. Monthly low flow runoff values for the study area (data compiled from U.S. Geological Survey, 2004a)

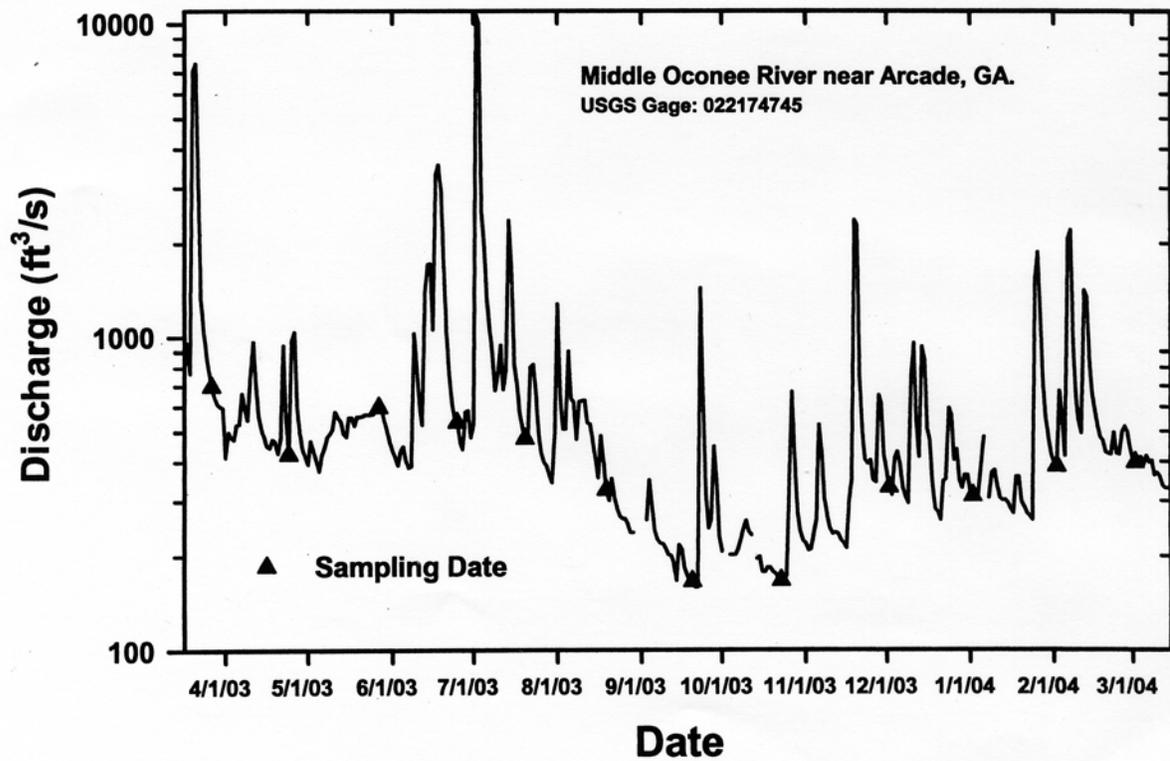


Figure 5. Hydrograph for Middle Oconee River near Arcade, Ga. during the study period showing sampling dates

Geological Survey, 2004b; Figure 5). Discharge values are transmitted from this site on a continuous basis through telemetry which facilitated sampling the Middle Oconee River and its tributaries under base flow or near-base flow conditions (i.e. periods between storm events when discharge was at a minimum; Figure 5). An assumption made for this study is that relative rates of discharge for the Middle Oconee River (the gaged stream) also apply to the three other ungaged stream locations that were monitored. This assumption is believed to be valid in that the streams are within ≈ 15 km of one another (Figure 1) and none of the discharge within this basin is regulated by dams. Stream water samples were collected using a weighted acid-washed, 18 M Ω DI-rinsed polyethylene collection vessel placed near the centroid of flow. Both stream water and ground water samples were transferred to acid-washed, DI-rinsed, sample-rinsed polyethylene sampling bottles and refrigerated until the analyses could be made.

A 5-centimeter diameter PVC monitoring well was installed to a depth of 17 meters on a wooded site adjacent to the Middle Oconee River near Jefferson, Georgia (Figure 1). This was the one undeveloped location permitted for drilling by the Jackson County Water and Sewage Authority. The well was auger-drilled and a 5-meter long, 20-slot PVC well screen was installed at the bottom of the well. No extraneous fluids were introduced for its construction or development. The water table was located at a depth of approximately 8 meters below land surface and varied by < 1 meter during the duration of this study. Soil samples were taken from the auger bore at 1.5-meter intervals and were found to be uniformly comprised of dark brownish red sandy clay, characteristic of ultisols. The newly installed well was allowed to equilibrate with ground water for one month and during each sampling period one well volume was extracted with a polyethylene bailer immediately before the final sample was taken.

Major Ion Analytical Methods:

The specific conductance of the ground water and stream water was measured in the field using a YSI conductivity meter. The pH and alkalinity was measured on unfiltered samples using an Orion 720 pH meter (buffered at pH = 4.0 and 7.0) and 0.02N H₂SO₄ titrant. The precision associated with the titration was 6% as one relative standard deviation (rsd) [A relative standard deviation = 1 standard deviation/mean]. Non-acidified samples were used for anion analyses and were filtered first through 0.45μ acetate membrane and then through a 0.20μ membrane. Chloride and sulfate concentrations were determined using a Lachat 5000 ion chromatograph (bicarbonate/carbonate eluent; rapid anion method). The precision associated with these measurements was better than 5% (1 rsd). Cation concentrations (K, Na, Ca, Mg) were measured upon 0.45μ filtered, acidified (pH < 2.0) samples using a Perkin Elmer 3110 atomic absorption spectrophotometer. Magnesium ion concentrations were focused upon in this present study in that the precision associated with these measurements is better than 4% (1 rsd).

Tritium and Stable Oxygen Isotopes:

Tritium concentrations were measured at the University of Waterloo's Environmental Isotope Laboratory by a beta particle counting method following electrolytic pre-concentration of tritium within the samples. Tritium concentrations are reported in tritium units (T.U.), where 1 T.U. = 1 tritium atom in 10¹⁸ hydrogen atoms in water. Replicate measurements of several water samples indicated a repeatability within 1.5 T.U. Stable oxygen isotopes were measured at the Geochron Laboratories using a CO₂ equilibration method. The precision associated with these measurements is \pm 0.2 per mil. The results are reported as $\delta^{18}\text{O}$ per mil relative to SMOW (Standard Mean Ocean

Water) where:

$$\delta^{18}\text{O}_{(\text{SMOW})} = \left\{ \left[\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{Sample}} - \frac{^{18}\text{O}}{^{16}\text{O}}_{\text{SMOW}} \right] \times \left[\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{SMOW}} \right]^{-1} \right\} \times 1000$$

Strontium Ion Concentrations and Strontium Isotope Ratios:

Strontium ion concentrations and isotopic ratios were measured at the University of North Carolina-Chapel Hill mass spectrometry laboratory under the direction of Dr. Paul Fullagar. The determinations were performed on a Micromass Sector 54 thermal ionization mass spectrometer (TIMS). Typically this laboratory is able to measure strontium (Sr) ion concentrations with a precision and accuracy of better than 1% (Woods et al., 2000). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were adjusted using National Bureau of Standards #987 as to conform to a well-recognized standard. The percentage error associated with these measurements is <0.0010 and therefore the isotopic ratios are typically significant to the 5th decimal place (however in most cases they are reported only to the fourth decimal place).

RESULTS

Hydrology:

The study area received 57.8 inches (1467 mm) of precipitation between April 1, 2003 and March 31, 2004 (Appendix 1). This is 21% greater than normal for an annual period and most of the excess precipitation occurred during June and July, 2003 when precipitation was three to five times greater than normal. Average daily discharge for the Middle Oconee River near Arcade during the study period varied between 167 cubic feet per second (cfs) and 10,800 cfs (Appendix 2). The total discharge for the study period was 37% greater than normal with the excess primarily limited to the exceptionally wet period between June and July, 2003 (Figure 6).

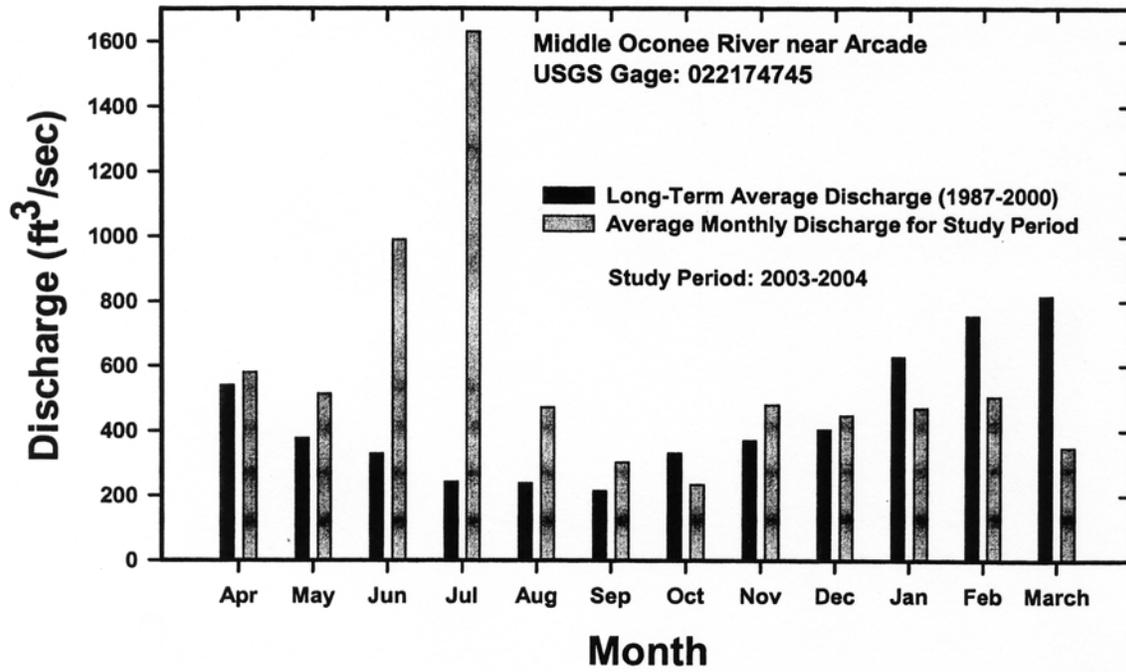


Figure 6. Monthly discharge data for the Middle Oconee River near Arcade, Georgia

During the later portion of the study period, between September, 2003 - March, 2004, discharge rates were near or below normal (Figure 6) and it was during this period that base flow dominated. Average base flow rates during the first four months of the study period (April-July, 2003) were \approx 400 cfs and then declined by nearly a factor of two to 200 cfs during the period. Monthly discharge data for the Middle Oconee River near Arcade, Georgia between August-December, 2003 (Figure 5). During the later part of the study period base flow rates rose to near their level at the beginning of the study period. As previously discussed, this decline in base flow rates during the hot summer months is a defining characteristic of stream flow in this region and is a result of potential evaporation exceeding precipitation. However, due to the excessive summer rain during this study period, the decline in base flow rates was slightly less than average for both the Middle Oconee River and the region as a whole (as defined by the nine Piedmont streams for the period 1987-2002; Figure 4).

Tritium(³H) Concentrations:

Tritium concentrations varied between 7.3 and 16.6 T.U. and the average was 10.2 T.U. for base flow in the four stream basins (Table 2, Appendix 3). The average concentration in shallow ground water was 15.8 T.U. In contrast, the average weighted rainfall concentration for the study period was 7.2 T.U. and 5.1 T.U. for the period between 1999 - 2002 in the Panola Mountain research watershed located \approx 45 km southeast of the study area (written communication, Robert L. Michel, 2003). Environmental tritium values within base flow and shallow ground water that are higher than precipitation values are consistent with the presence of some pre-bomb and bomb-period water (Rose, 1993 and Rose, 1996) as will be subsequently discussed. Tritium concentrations were also approximately 10 units lower within these stream

Table 2
Statistical Summary of Major Ion Chemistry and Isotopic Parameters

Middle Oconee River near Arcade, Georgia (USGS gage number: 022174745)								
	Specif. Cond.(μS/cm)	pH	Alkalinity (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	$\delta^{18}\text{O}$ SMOW	^3H (T.U.)
Low	70.0	6.00	24.4	1.8	2.1	4.8	-6.0	7.3
High	92.3	7.08	33.3	2.0	8.7	11.0	-5.1	14.0
Average	81.9	6.70	27.7	1.9	5.4	7.7	-5.4	9.1
Standard Deviation	6.1	0.29	2.9	0.1	1.8	2.5	0.3	2.3
Rel. Std. Dev. (RSD)	7.4%	4.4%	10.5%	5.7%	32.8%	33.2%	5.7%	25.0%
Number	12	12	12	12	12	12	11	8
Pond Fork Creek								
	Specif. Cond.(μS/cm)	pH	Alkalinity (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	$\delta^{18}\text{O}$ SMOW	^3H (T.U.)
Low	66.2	6.36	22.7	1.6	1.8	4.8	B5.7	9.0
High	76.9	7.06	30.5	1.9	3.8	10.1	-4.9	11.1
Average	74.3	6.82	26.5	1.8	2.1	7.3	-5.2	10.1
Standard Deviation	3.8	0.22	2.7	0.1	0.6	2.1	0.3	0.8
Rel. Std. Dev. (RSD)	5.1%	3.2%	10.2%	5.6%	29.9%	30.7%	5.0%	7.5%
Number	12	12	12	12	12	12	8	6

Table 2 (continued)
Statistical Summary of Major Ion and Isotopic Parameters

Indian Creek (1st order)								
	Specif. Cond.(μS/cm)	pH	Alkalinity (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	$\delta^{18}\text{O}$ SMOW	^3H (T.U.)
Low	86.9	6.53	30.5	1.4	1.1	5.1	-5.4	7.6
High	112.2	7.06	47.2	1.8	3.7	14.4	-4.8	16.6
Average	92.6	6.56	35.9	1.6	2.1	10.5	-5.1	15.8
Standard Deviation	9.9	0.25	4.7	0.2	0.7	3.4	0.2	3.2
Rel. Std. Dev. (RSD)	10.6%	3.8%	13.2%	10.7%	34.6%	32.3%	4.8%	19.9%
Number	11	11	11	10	11	11	9	6
Indian Creek (2nd order)								
	Specif. Cond.(μS/cm)	pH	Alkalinity (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	$\delta^{18}\text{O}$ SMOW	^3H (T.U.)
Low	59.5	6.38	26.0	1.8	1.2	5.5	-5.4	10.5
High	84.8	7.01	36.6	2.0	2.6	11.6	-4.4	11.1
Average	78.4	6.74	30.6	1.9	2.1	7.9	-5.0	10.8
Standard Deviation	7.1	0.22	3.5	0.1	0.5	2.4	0.4	0.4
Rel. Std. Dev. (RSD)	9.1%	3.2%	11.3%	4.2%	23.0%	31.0%	7.1%	3.7%
Number	11	11	11	11	11	11	8	2

Table 2 (continued)
Statistical Summary of Major Ion and Isotopic Parameters

Shallow Ground Water								
	Specif. Cond. (μS/cm)	pH	Alkalinity (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	δ¹⁸O SMOW	³H (T.U.)
Low	15.2	4.89	2.7	0.4	0.2	<0.2	-6.1	12.2
High	32.2	5.29	6.1	0.5	0.9	4.3	-5.4	20.5
Average	21.0	5.17	4.0	0.5	0.6	2.9	-5.6	15.8
Standard Deviation	5.5	0.13	1.4	0.04	0.2	1.5	0.3	3.2
Rel. Std. Dev. (RSD)	25.9%	2.5%	34.6%	7.8%	38.5%	50.5%	5.0%	19.9%
Number	7	7	7	7	7	7	5	5

waters than they were a decade ago in the nearby Upper Ocmulgee River basin (Rose, 1993), consistent with radioactive decay rates.

The average tritium concentrations in base flow for the four watersheds varied only between 9.1 T.U. (Middle Oconee River) and 11.5 T.U. (first-order tributary of Indian Creek) during this study period. Two-tailed t-tests ($\alpha = 0.05$) indicate that there is no statistically significant difference between the average tritium concentration between Pole Branch Creek, Indian Creek (first-order tributary), and the Middle Oconee River near Arcade. There is no apparent relationship between tritium concentrations in base flow and watershed area. This suggests that all four watersheds process rainfall in a similar manner and that the average residence times of ground water comprising base flow in the four watersheds are also similar. The greatest temporal variability was observed for the Middle Oconee River as defined by the relative standard deviation (rsd) of 25.0% and the Indian Creek first-order tributary (rsd = 25.5%). However, this variation was apparently random and was not associated with consistent seasonal trends (Figure 7); therefore the causes of these variations are not readily identifiable. This stands in contrast to an earlier study by Rose (1993) in which tritium concentrations in stream water from the Upper Ocmulgee basin (≈50 km from the Middle Oconee River basin) were seasonal and decreased during the wetter portion of the year. During the early 1990's tritium concentrations in stream base flow were also significantly higher (18-30 T.U.) which may explain why the seasonal trend was no longer apparent.

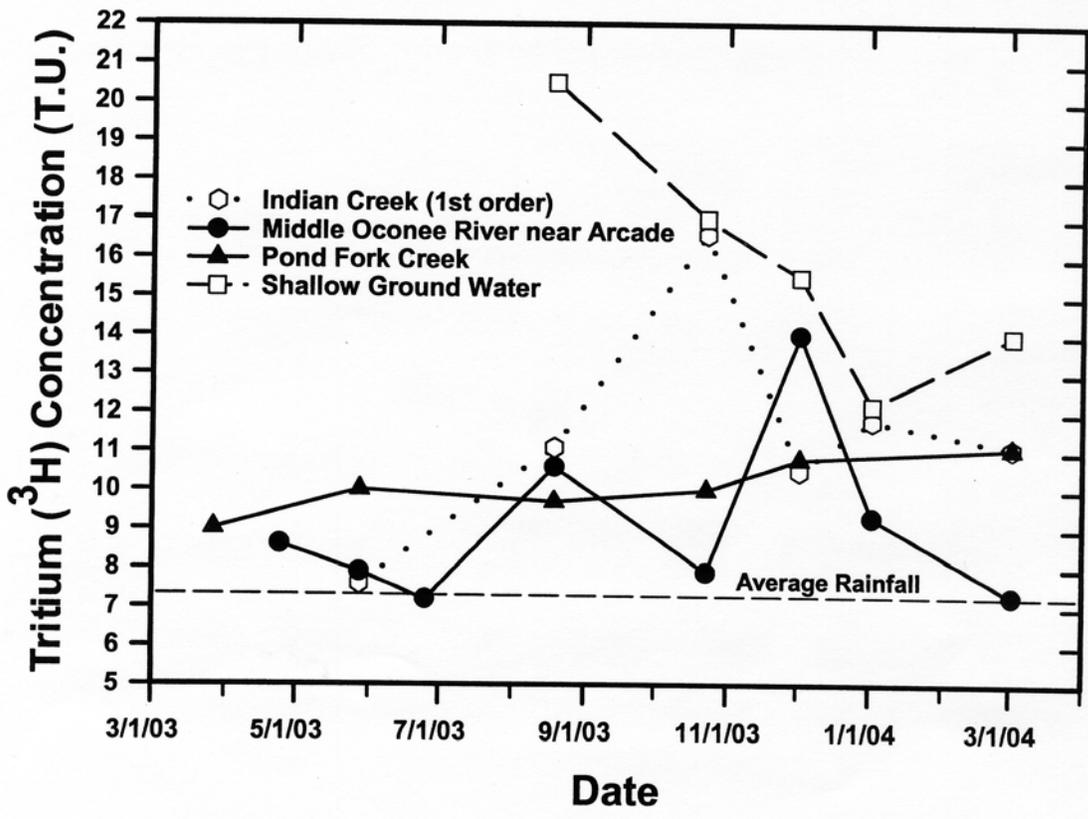


Figure 7. Environmental tritium concentrations within base flow and shallow ground water in the Middle Oconee River basin

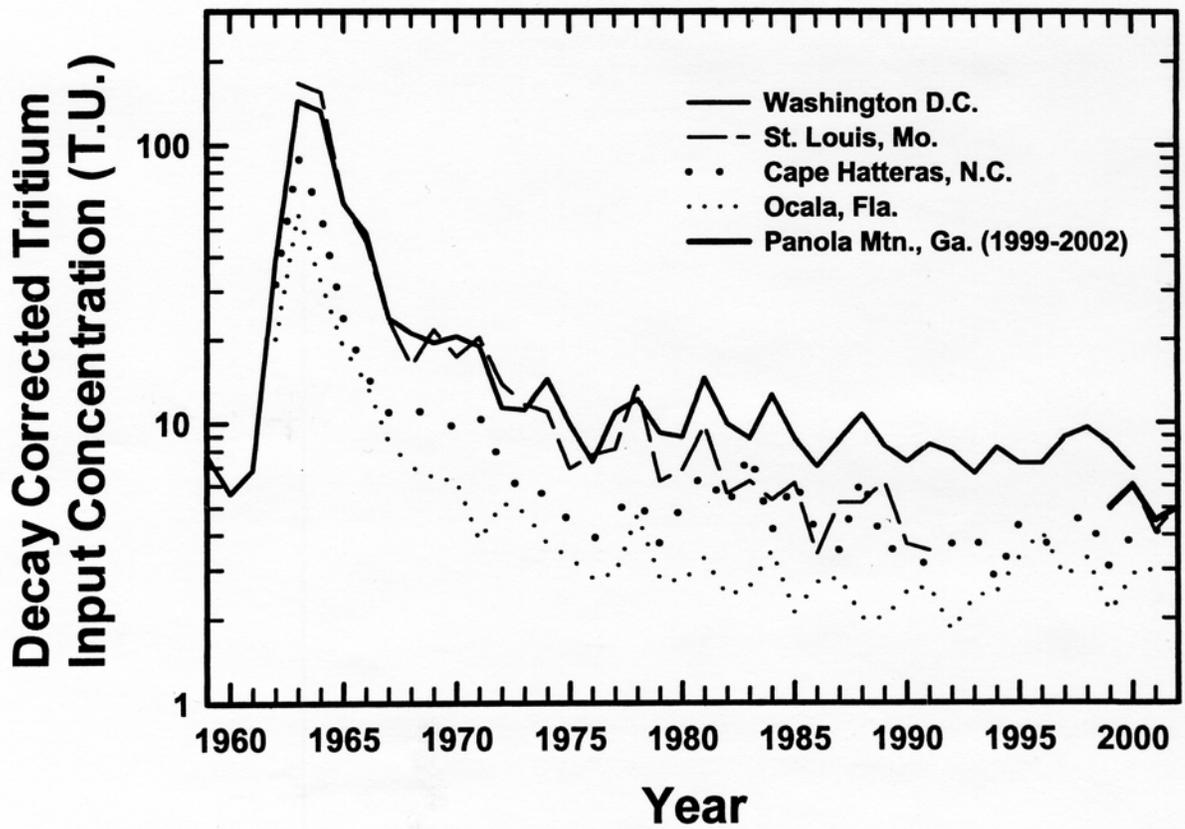


Figure 8. Decay-corrected tritium input concentrations within rainfall for the southeastern United States

Table 3
Decay Corrected Tritium Concentrations in Southeastern U.S. Rainfall
(Values are in Tritium Units [T.U.]

Period	Rainfall Collection Location				
	Washington D.C. ¹	St. Louis Mo. ¹	Cape Hatteras ¹	Ocala, Fla. ¹	Northeastern Ga ^{1,2}
2002-1993	7.9	5.0	3.9	2.8	6.1
2002-1983	8.8	5.5	4.3	2.7	No data
2002-1973	9.6	6.0	4.6	3.3	No data
2002-1963	20.0	21.0	10.1	6.6	No data
¹ International Energy Association data - compiled by Robert L. Michel, U.S. Geological Survey (written communication) ² Data obtained by Rose (1996)					

There was a statistically significant difference (t-tests; $\alpha=0.5$) between tritium values in shallow ground water (average tritium concentration = 15.8.3.2 T.U.) and the stream base flow (average tritium concentration = 10.2.2.2 T.U.). This (along with other parameters to be discussed later) indicates that the base flow cannot be equated with the shallow ground water that was monitored as part of this investigation. Decay corrected tritium input concentrations in southeastern rainfall have generally been between 5-10 T.U. for the past 10 years (Figure 8 and Table 3). In order to account for the higher values observed in shallow ground water (average tritium concentration= 15.8 T.U.) there would likely have to be a component of bomb-test water (i.e. decay-corrected rainfall from the middle 1960's) in the shallow ground water mixture.

Base flow tritium concentrations (average = 10.2 T.U.) are lower than the shallow ground and more closely resembled modern rainfall values (between 5.1 - 7.2 T.U. as measured in this study). The higher values in the ground water initially suggest that it might have a longer average residence time than base flow within the four streams in that tritium concentrations in rainfall have declined during the past 40 years from their peak bomb test values of the mid-1960's (Figure 8). This interpretation, while possibly consistent with the tritium data itself, is probably not correct in that the shallow ground water is characterized by a relatively low pH and specific conductance (see subsequent discussion of stream chemistry). In fact the low ionic loads present in shallow ground water much more closely resemble rain water than they do base flow. Therefore, it would be very problematic to imply that the shallow ground water has a lower percentage of more recent rainfall or that it has a greater residence time than the ground water that comprises base flow in the Middle Oconee River basin.

One possible explanation for these results is that the base flow consists of a mixture of post-bomb (i.e. water from the past 30 years), bomb-test, and some pre-bomb (i.e. > 40 year old)

recharge. The older pre-bomb input would have decay-corrected tritium values that are nearly zero and therefore the higher percentage of pre-bomb waters, the lower the total ^3H concentration of the base flow mixture. It should be emphasized that this argument is somewhat speculative and other explanations may be possible. However, it is very clear that both shallow ground and base flow are more tritiated than southeastern U.S. rainfall has been during the past two to three decades. This suggests a decade-scale residence times for both the shallow ground water and the base flow, consistent with previous interpretations of the residence time of natural waters in the Georgia Piedmont Province (Burns et al., 2003, Rose, 1996, and Rose, 1993).

Stable Oxygen Isotope Ratios ($\delta^{18}\text{O}$ relative to SMOW):

The stable oxygen isotope ratios measured in precipitation samples collected in Decatur, Georgia during the study period averaged -5.4 per mil (as a weighted value) and varied between -8.1 and -1.8 per mil (Appendix 4; Table 2). The high degree of variability between rainfall samples can be inferred from rsd value of 31.8% for the 13 samples (Appendix 4). In contrast, the $\delta^{18}\text{O}$ composition of stream base flow varied between -6.1 and -4.8 per mil during the study period (Table 2). The four-stream average base flow composition (-5.2 per mil) was similar to but slightly heavier than the average ground water value ($\delta^{18}\text{O} = -5.6$ per mil). Both the ground water and stream base flow average values were within the analytical error of weighted rainfall (-5.4 per mil). There was no apparent relationship between $\delta^{18}\text{O}$ values (and their relative standard deviations) and stream order or watershed size. This indicates (as does the previously discussed tritium data) that rain water is processed in a similar manner in all four watersheds irrespective of their basin area. The isotopic variation observed in the four streams during the year-long study period (Figure 9) is slightly greater than the analytical error associated with these measurements

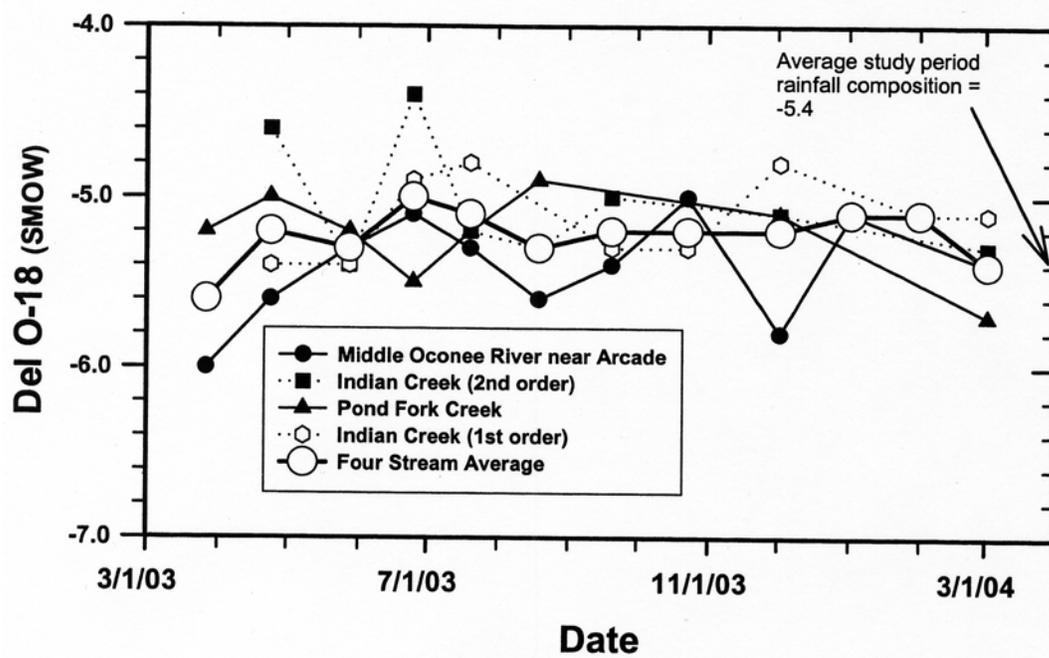


Figure 9. $\delta^{18}\text{O}$ values in base flow within the Middle Oconee River basin

(. 0.2 per mil) indicating that base flow is not, however, a completely temporally invariant, homogenous mixture. Unfortunately the hydrological significance of this isotopic variation is not precisely clear.

If rainfall is collected on a regular basis over a multi-year period, lighter isotopic ratios would be observed in winter precipitation than during the remainder of the year (Gat, 1980). Using the relationship between stable oxygen isotope compositions and monthly mean air temperatures compiled by Yurtsever (1975), winter rainfall in the southeastern U.S. is ≈ 5 per mil lighter than summer rainfall. Lighter isotopic ratios were not observed in stream base flow during the winter months which indicates that there was not a significant contribution of seasonal rainfall within base flow. The relative standard deviations associated with stable oxygen isotopic composition of base flow varied only between 4.8 and 7.1% for the four watersheds, very similar to the relative standard deviation of 5.0% associated with the shallow ground water. The similarity between the ground water rsd values and the base flow values suggests that seasonal isotopic variation becomes homogenized at shallow depths (i.e. < 15 meters) within the soils. The relative standard deviations for base flow and shallow ground water are very modest compared to the rsd values associated with rainfall (31.8%) and are consistent with the isotopic homogenization reported by Wenner et al. (1991) in a similar watershed in the Georgia Piedmont. The lack of seasonal variation and isotopic homogeneity is also consistent with the multi-decade residence time of ground water (both shallow ground and ground water comprising base flow) inferred from the tritium data.

Major Ion Geochemistry:

Major ion concentrations in base flow in all four basins were characteristically low as indicated by specific conductance values that ranged between 59.5 - 112.6 $\mu\text{S}/\text{cm}$ and averaged 81.8 $\mu\text{S}/\text{cm}$ (Table 2). These relatively low values are typical of the Georgia Piedmont which is underlain by rock comprised of relatively insoluble aluminosilicate minerals. The specific conductance of shallow ground water was considerably lower than the stream base flow and ranged between 15.2 - 32.2 $\mu\text{S}/\text{cm}$. This clearly indicates that the shallow ground water (i.e. < 17 meters) is not representative of base flow in this study area. The first-order Indian Creek stream was characterized by the highest solute loads with an average specific conductance of 92.6 $\mu\text{S}/\text{cm}$ (Table 2). The relatively high solute concentrations are consistent with the land use (horse pastures) that is characteristic of most of this 3.9 km^2 basin. The relative standard deviations for specific conductance in the four streams varied between 5.1 - 10.6% and were highest for the first-order Indian Creek watershed (Table 2).

The pH of base flow remained near neutral on a year-round basis varying between 6.00 and 7.08 and averaged 6.71 within the four basins (Table 2). The shallow ground water was more acidic and ranged between 4.89 - 5.29 during the study period. Magnesium concentrations, an indicator of biotite and hornblende dissolution, varied between 1.4 - 2.0 mg/L and averaged 2.0 mg/L within base flow from the four streams. Magnesium ion variation was not seasonal and relative standard deviations varied between 4.2 - 10.7% in stream base flow (Table 2), values that exceed the analytical imprecision.

Bicarbonate (as determined by alkalinity titration) is the dominant ion in these waters and concentrations ranged between 22.7 and 44.2 mg/L and averaged 30.2 mg/L. In contrast, the average magnesium ion and bicarbonate alkalinity concentrations in shallow ground water were 0.5 and 4.0 mg/L (Table 2). The relative standard deviation for bicarbonate alkalinity in base flow varied between 10.2-13.0%, also reflecting a degree of variability greater than analytical uncertainty. Alkalinity variation was somewhat seasonal and during the period between August and November, 2003 when discharge values were lowest (Figures 5 and 6), average alkalinity concentrations in base flow for the four streams increased by 25% (Figure 10). This seasonal variation is likely real; however, it is difficult to infer from the yearly pattern of any single stream.

Surprisingly, this seasonal variation is not co-systematic with specific conductance values in that the four-stream average specific conductance decreased during the same August-November period (Figure 11) when alkalinity concentrations increased. It is also apparent that specific conductance values for base flow did not vary as a function base flow discharge as can be inferred from the plots and related regression coefficients shown on Figure 12. Sulfate and chloride concentrations respectively ranged between 1.1 - 8.8 and 4.8 - 14.4 mg/L within stream base flow (Table 2). The upper values for these parameters likely represent some measure of contaminative input from horse pastures, fertilizer, sewage effluent and/or septic tank leakage. Seasonal relationships or relationships between chloride and sulfate concentrations and basin area are hard to infer from these data.

F-Tests for Significance of Difference with Respect to Variance:

As previously detailed (Table 2 and Appendix 5) there is at least a moderate range of temporal variation for most of the chemical and isotopic parameters for a given watershed. This is reflected in relative standard deviations that are often greater than 10%. These variations may reflect some combination of random analytical error, seasonal factors effecting water flux within a watershed and variable contaminant inputs that have occurred upstream of a given sampling location.

In order to better understand the temporal variations within these data sets, one-tailed F-tests ($\alpha = 0.05$) were utilized to determine whether there were significant differences with respect to the variance (or standard deviation) for a given parameter between watersheds. The set of parameters included magnesium, chloride, specific conductance, bicarbonate alkalinity, $\delta^{18}\text{O}$, and tritium concentrations. The results of these tests are summarized in Table 4 and they indicate that there are only a few parameters in which the variances between watersheds for a given parameter are significantly different. Most of these differences relate to the first-order tributary of Indian Creek (watershed area = 3.9 km^2) in which the variance for magnesium, alkalinity, specific conductance and a few other parameters were significantly larger than the larger watersheds. It might be expected that the smallest or least buffered of the watersheds would be more subject to temporal variation and therefore have the highest associated variances. The temporal variation might result from differential water flux through the basin and contamination inputs from the land surface. There was very little difference with respect to variance between the three larger watersheds which may indicate that similar buffering and/or mixing processes occur on a watershed scale that is greater than $\approx 10 \text{ km}^2$. This observation while relevant to the

Middle Oconee River drainage basin should not be construed as a hard-and-fast rule for all Piedmont Province watersheds.

Strontium Ion Concentrations and Isotope Ratios:

Strontium ion concentrations ranged between 16.3 - 26.9 $\mu\text{g/L}$ (Table 5) in base flow from the four Middle Oconee River basin streams. These values are relatively low compared to the global river average of 78 $\mu\text{g/L}$ (Palmer and Edmond, 1992) and can likely be attributed to the limited input of strontium from carbonate minerals within these aluminosilicate watersheds. The base flow concentrations strontium concentrations were, however, much greater than those in rainfall (1.4 - 4.0 $\mu\text{g/L}$) and shallow ground water (5.2 - 7.1 $\mu\text{g/L}$; Table 5) indicating a strong weathering component of strontium in the stream water. There was little temporal strontium variation within base flow for a given stream as evidenced by relative standard deviations that varied between 4.1% and 12.3% and the strontium concentrations were very similar in each of the streams (Table 5). The only statistically significant differences (two tailed t-tests, $\alpha = 0.05$) between mean strontium ion concentrations were between Pond Fork Creek and the two Indian Creek tributaries and this difference was only $\approx 3 \mu\text{g/L}$. This indicates that the reactions controlling the strontium ion influx were quite similar throughout the 860 km^2 study basin.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios varied between 0.7113 - 0.7176 and averaged 0.7145 within base flow in the four stream basins (Table 5). This average is more radiogenic than the global average for river water which is 0.7119 (Palmer and Edmond, 1992). The average ratio is very close to the whole-rock ratio of 0.7140 observed for the granodiorite rocks at the nearby Panola Mountain research watershed (White et al., 2001).

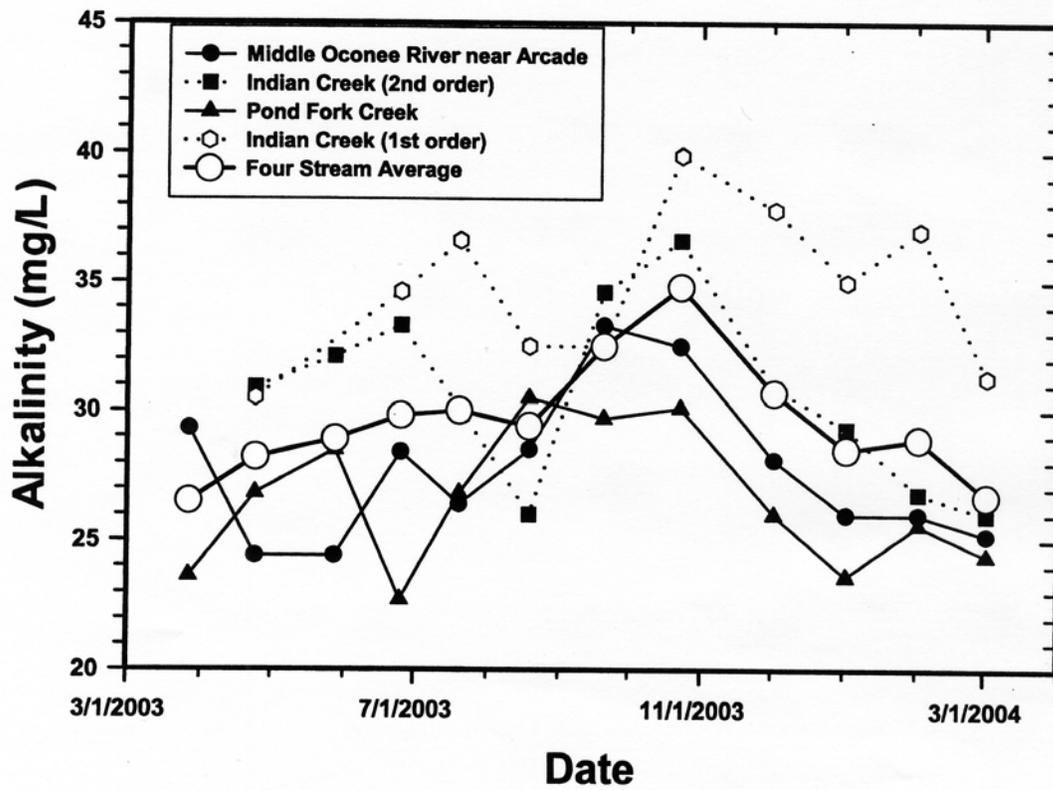


Figure 10. Alkalinity concentrations in base flow within the Middle Oconee River basin

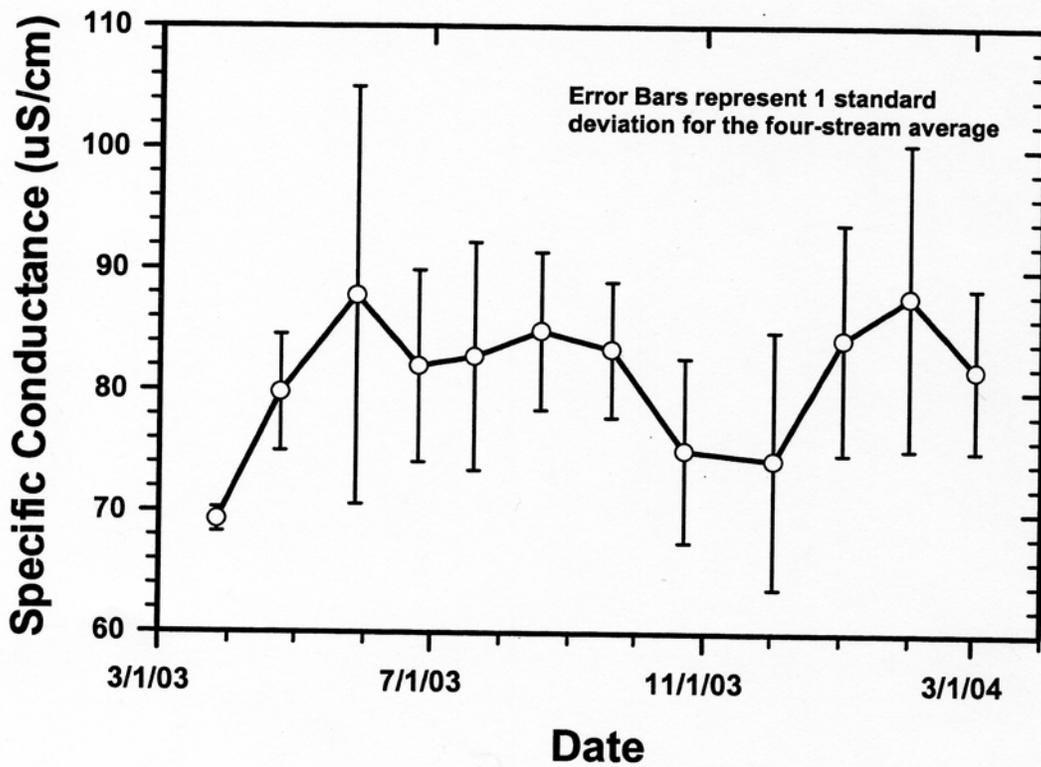


Figure 11. Average specific conductance values in base flow in the Middle Oconee River basin

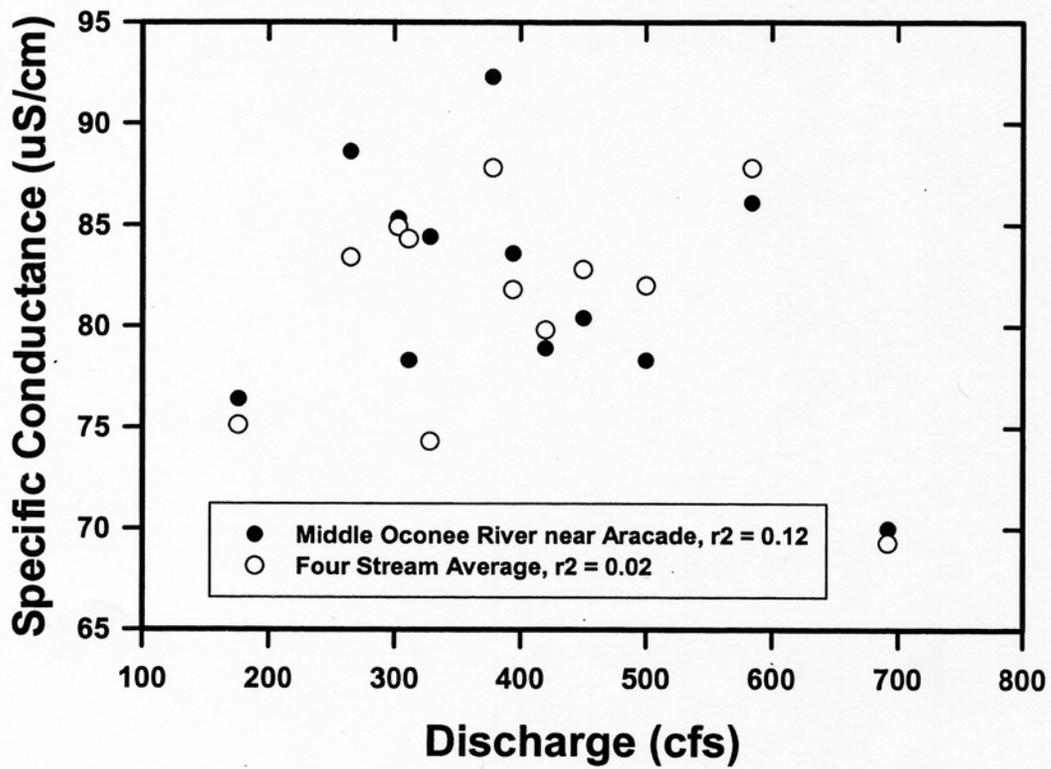


Figure 12. Relationship between specific conductance and discharge in base flow within the Middle Oconee River basin

Table 4
Summary of F-test Results for Stream Base Flow and Shallow Ground Water⁽¹⁾

	Indian Creek (first order)	Indian Creek (second order)	Pond Fork Creek	Middle Oconee River near Arcade	Shallow Ground Water
Indian Creek (first order)					
Indian Creek (second order)	Magnesium, $\delta^{18}\text{O}$				
Pond Fork Creek	Magnesium, Specific ⁽²⁾ Conductance, Alkalinity, Tritium	Alkalinity		Tritium	Tritium
Middle Oconee River near Arcade	Magnesium	Magnesium			
Shallow Ground Water	Magnesium, Specific Conductance, Alkalinity, Chloride	Alkalinity	Magnesium	Magnesium, Bicarbonate	

⁽¹⁾ These are one tailed F-tests ($\alpha = 0.05$)
Parameters tested: Magnesium, Chloride, Specific Conductance, Bicarbonate Alkalinity, $\delta^{18}\text{O}$, and Tritium

⁽²⁾Explanation: The parameters in the box are those for which the standard deviation for the sampling point represented in the row is significantly ($\alpha = 0.05$) greater than the sampling point represented in the column (i.e. the standard deviation for magnesium, specific conductance, alkalinity, and tritium is greater within the sampling set for Indian Creek - first order tributary than the sampling set for Pond Fork Creek).

The relatively high ratios are consistent with the dominance of aluminosilicate minerals, particularly the Rb-bearing biotite within schists that are a dominant rock type in these watersheds. The substitution of Rb for K-feldspar may be another significant source of The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for all base flow were statistically significant at a very high level of confidence (two-tailed t-tests, $\alpha = 0.00001$) indicating that each stream is characterized by its own strontium isotopic signature. The highest ratios were observed in the terminal Middle Oconee River basin ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{average}} = 0.7172$) and the lowest ratios were observed in the two small Indian Creek watersheds ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{average}} = 0.7127$ and 0.7133)

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in base flow for all four streams were extremely consistent over the duration of the 12-month sampling period (Figure 13). The average difference between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the four streams ($n = 35$) between consecutive sampling periods was 0.000098 which is 40 times less than the average analytical error for this set of samples. This is not true for the ground water samples in which the average difference between the sampling periods exceeded the analytical error. The time-invariance with respect to Sr-isotope ratios is also reflected in the relative standard deviations for base flow which varied only between 0.01% - 0.02%. In comparison, the relative standard deviations for the shallow ground water and weighted rainfall were 0.07% and 0.08%, respectively. Strontium ion concentrations also varied little between sampling periods as evidenced by rsd values of <5% in three of the four streams (Table 5). In contrast, the rsd values for magnesium in stream base flow varied between 4-11% (Table 2) and magnesium was the most time-invariant major ion parameter with a total range of base flow variation between 0.2 - 0.4 mg/L. Relative standard deviations for the strontium

isotope ratios are likewise ~50 times less than rsd values for ratios of the major ions (e.g. Mg/HCO₃) in base flow.

Strontium ion concentrations and isotope ratios have undergone a discernable evolution within the Middle Oconee River watershed. Strontium concentrations in rainfall are very low (i.e. < 5 ppb) and ⁸⁷Sr/⁸⁶Sr ratios are also low (<0.7125, Figure 14). Strontium ion concentrations increase slightly in shallow ground water to values between 5-8 ppb); however, the isotopic ratios remain very similar to rain water. A likely source of strontium is ion exchange or desorption from the clay minerals and iron oxyhydroxides comprising the ultisols. The shallow

Table 5
Summary of Strontium Ion Concentrations and Isotope Ratios

Strontium Ion Concentrations						
	Middle Oconee River	Pond Fork Creek	Indian Creek (1st order)	Indian Creek (2nd order)	Shallow Ground Water	Rainfall (unweighted)
Low	16.3	20.1	22.6	23.2	5.2	1.4
High	26.9	23.3	26.3	26.2	7.3	3.3
Average	23.6	21.8	24.1	24.2	6.1	2.5
Std. Dev.	2.9	1.1	1.0	1.0	0.9	1.1
Rel. Std. Dev.	12.3%	4.9%	4.2%	4.1%	15.4%	44.8%
Number	11	8	9	8	6	5
Strontium Isotope Ratios (⁸⁷Sr/⁸⁶Sr)						
	Middle Oconee River	Pond Fork Creek	Indian Creek (1st order)	Indian Creek (2nd order)	Shallow Ground Water	Rainfall (unweighted)
Low	0.71698	0.71463	0.71329	0.71259	0.71113	0.71093
High	0.71757	0.71475	0.71343	0.71285	0.71251	0.71225
Average	0.71722	0.71470	0.71331	0.71271	0.71205	0.71174
Std. Dev.	0.00016	0.00004	0.00006	0.00009	0.00051	0.00057
Rel. Std. Dev.	0.02%	0.01%	0.01%	0.01%	0.07%	0.08%
Number	11	8	9	8	6	5

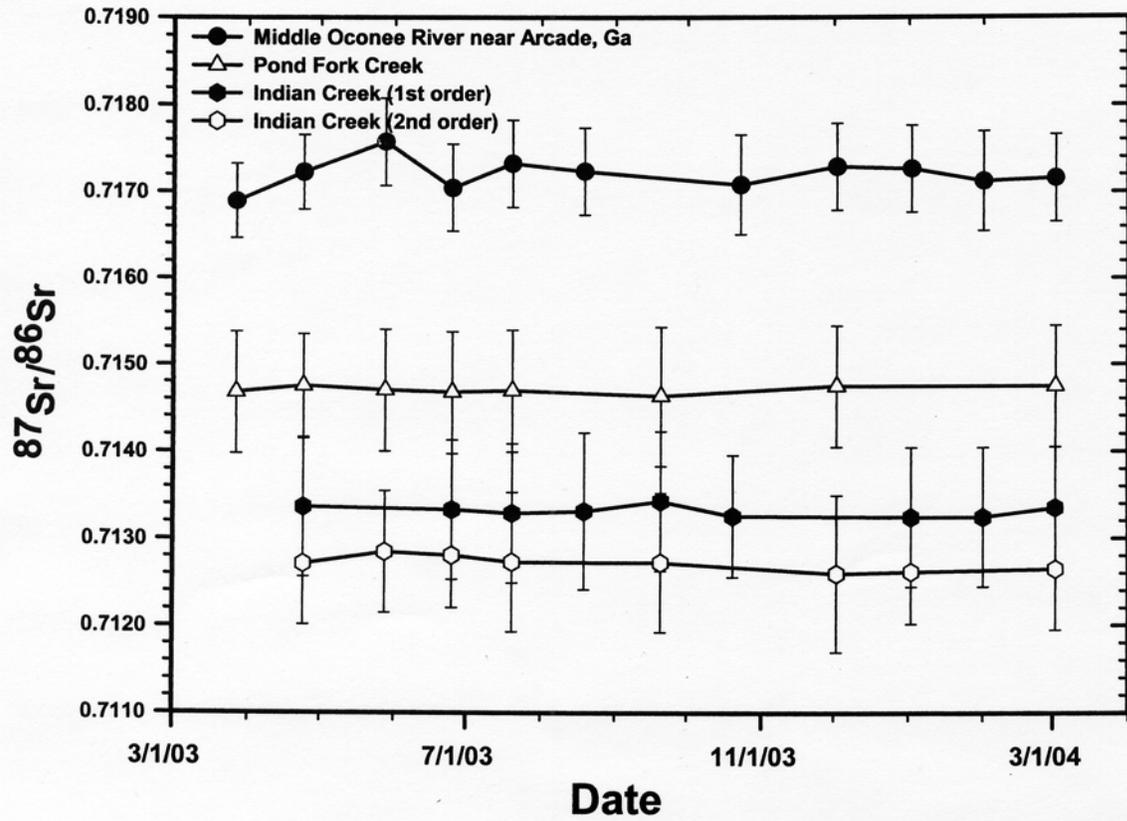


Figure 13. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in base flow within the Middle Oconee River basin

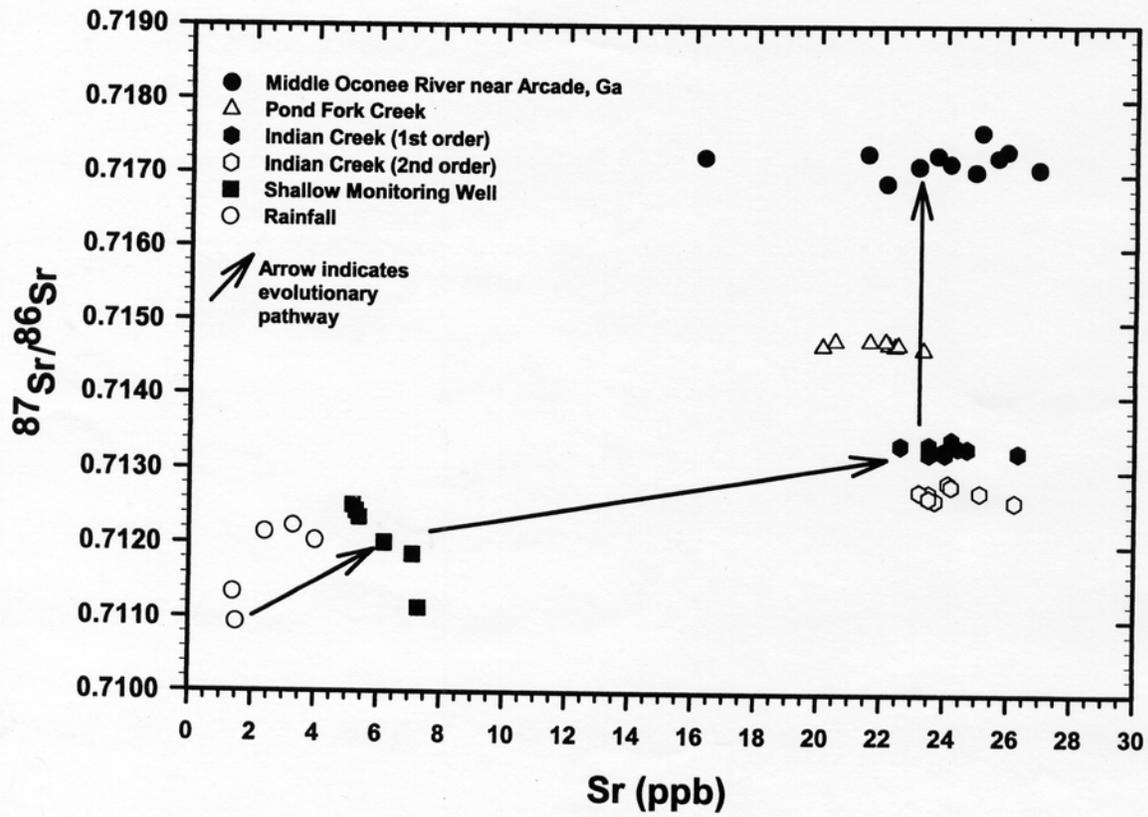


Figure 14. Evolutionary pathway for strontium isotopes in the Middle Oconee River basin

ground water is only mildly acidic ($4.9 < \text{pH} < 5.3$) and therefore strontium should be fairly stable on soil exchange sites. As weathering proceeds, strontium ion concentrations increased to approximately 25 ppb in stream base flow and each watershed retains a near-constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, seemingly independent of water flux (discharge) and other factors that affect a range of temporal variation for other chemical parameters such as alkalinity and total solute loads. Other investigations (i.e. Land et al., 2000) have also observed that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are considerably lower within the shallow subsurface and then increase as weathering processes add increased proportions of strontium-87 to the mixture.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were observed to increase with increasing watershed area while total strontium concentrations remain nearly constant independent of watershed area, land use, and other factors (Figure 14). Pollution from the horse-pasture in the small Indian Creek watershed does not have a discernable effect upon strontium ion concentrations. A possible explanation for this evolutionary trend with respect to increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios might involve a variable source area effect in which larger basins acquire their solute composition from a slightly different and more expanded set of minerals than the smaller basins. It may be that base flow in the larger basins acquires a higher percentage of solutes from more recalcitrant or low-solubility minerals such as potassium feldspar which have a more radiogenic or higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

DISCUSSION

Seasonal Variations with Respect to Rates of Base Flow Influx:

Probably the most important aspect of base flow within the Middle Oconee River watershed for scientific consideration is that it is seasonally variable and that on average it

decreases by a factor of approximately three during the period of April through October (Figure 4) when a water deficit typically exists (Figure 3). During this study period it decreased only by a factor of two, presumably as a result of the extraordinary wet period that occurred from June - July, 2003. Seasonally variable low flow occurs throughout the Piedmont Province in the southeastern United States and has implications for water budgeting, resource planning, reservoir storage design and the maintenance of quantity and quality of water for irrigation, recreation, and wildlife conservation (Smakhtin, 2001).

One possible way to analyze this problem is to ask where does the additional water comes from during the cool months (i.e. why do base flow rates increase by a factor of ≈ 3 during the period between November and March?). Several hypothetical mechanisms for the additional base flow can be posed and analyzed; however, a definitive answer to this question is still elusive. The first mechanism involves the actual influx of seasonal precipitation and the outflux of this seasonal input through the watershed as base flow. This mechanism might involve increased production from the vadose zone and/or from the riparian zone near the stream itself. The second mechanism involves an increased hydraulic gradient during the November-March period, thereby increasing the ground-water discharge to the stream channel (which serves as a ground water sink). The third mechanism is similar to the first; however, it involves the outflux of previously stored water (i.e. non-seasonal or old water) to base flow during the high-flow period. Some combination of all three mechanisms is of course possible.

The first hypothesis involving the seasonal influx of new water can be evaluated using the data acquired in this study. As previously detailed, there was some variation with respect to the $\delta^{18}\text{O}$ ratios in the four Middle Oconee River watersheds analyzed in this study (Figure 9). However, most of this variation falls within the range of .05 per mil, far less than calculated

seasonal variation of 5 per mil in southeastern U.S. rainfall (Yurtsever, 1975). Furthermore, there was no seasonal trend observed in which the oxygen isotopic composition of base flow becomes progressively lighter during the winter months. This was the case for the total range of basin scales analyzed in this study.

The tritium concentrations measured in both ground water and base flow do not support new water as an important source for the additional seasonal base flow. As previously detailed, tritium concentrations observed in the shallow ground water and some of the base flow were often 5-10 T.U. higher than in recent rainfall. Furthermore, in order to account for these increased tritium concentrations there must be a significant component of base flow that was recharged during the bomb period and possibly before the bomb testing of the 1960's. In other words, the ground water that constitutes base flow has an average residence time of perhaps 20-40 years. This precludes the possibility of a significant component of very recent seasonal water within base flow. The significantly greater concentrations of dissolved solutes base flow compared to shallow ground water also indirectly indicate significantly longer residence times for the base flow. Furthermore, there are no isotopic data which indicate that the shallow ground water is comprised of seasonal recharge. Therefore, given these constraints, it is highly unlikely that the increased base flow during the relatively cool months of November-March is derived directly from the influx and outflux of seasonal precipitation; however, some small proportion of seasonal precipitation may be part of the total base flow mixture.

The second mechanism involves an increase of hydraulic gradients through the input of seasonal water which in turn increases the rate of ground water outflux in the form of base flow. This can be modeled by Darcy's Law as follows:

$$q = K \Delta h / \Delta L \quad [1]$$

where q is base flow discharge per unit cross-sectional area of stream bottom receiving base flow influent, K is the hydraulic conductivity of the soils and rocks comprising the ground-water flow system, and $\Delta h/\Delta L$ is the hydraulic gradient between the watershed divide (or an equivalent point in the subsurface) and the stream channel. The estimated flow path or length (ΔL) is 2,000 - 3,000 feet which is the average distance of a watershed boundary to a stream channel in the study area. The average hydraulic gradient is likely less than 0.04 which is the average topographic slope. Under these conditions, particularly considering the estimated flow length, it is not likely that hydraulic gradients can change radically enough during the high-flow period to increase the rate of discharge (q) by a factor of two or three. It should be noted that water levels observed within the monitor well varied by only ≈ 1.5 feet during the course of the study. In short, hydraulic heads are not likely to rise by the many feet required to account for these increased rates of discharge. However, it is likely that hydraulic heads near the riparian zone increase during the November-March period, accounting for some small proportion of the increased rate of ground-water discharge.

The third mechanism involves the release of previously stored water as base flow discharge during the high-flow period. This is a documented mechanism of water influx (McDonnell, 1990) that involves a decrease in soil tensions as the percentage of saturated pore space increases during the period of the year when precipitation rates exceed evaporation rates. The new water influx in turn releases water previously retained by considerable tension around the clay-rich soil matrix. Macro-pore flow through larger channels (if such exist) would augment this process and produce higher flow rates (McDonnell, 1990). As previously discussed, most of the geochemical, $\delta^{18}\text{O}$, and tritium data support the release of previously stored or non-seasonal

water as the most important mechanism accounting for the increased rates of base flow during the high-flow period.

Environmental Tritium and Stable Oxygen Isotope Variability and Basin Scale:

One of the primary objectives of this study was to identify and interpret the relationships that emerge between isotopic and geochemical variability and basin scale. The analysis of the environmental isotopes (those present as water in precipitation) which include tritium (^3H) and stable oxygen ratios ($\delta^{18}\text{O}$) indicates that the processing of rainfall through Piedmont Province watersheds is *not* strongly dependent upon basin scale. The average tritium concentrations within base flow for the four watersheds during the study period only varied between 9.1 and 10.8 T.U. These concentrations were significantly higher than recent rainfall (7-8 T.U.) and lower than shallow ground water (average =15.8 T.U.). The similarity of values between the basins and the differences between rainfall and shallow ground water speak to how similar each of the basins have processed rainwater during the past several decades.

As previously stated, the temporal variability at a given sampling location can be measured in terms of relative standard deviation for the total set of samples representative of that site. Hypothetically, smaller watersheds would be expected to produce higher rsd values than their larger counterparts because there is less storage capacity to buffer those changes brought about by variable atmospheric inputs. This relationship with respect to environmental tritium concentrations is not clear cut in that the highest rsd values (■25%) were observed for both the smallest watershed (Indian Creek - first order tributary; watershed area = 3.9 km²) and the largest watershed (Middle Oconee River near Arcade, Ga.; watershed area = 860 km²). The relative standard deviation for the set of tritium analyses for the intermediate sized watershed (Pond Fork

Creek; watershed area = 54 km²) was considerably lower at 7.5% (Table 2). The hydrological reasons for this dissimilarity are not readily apparent.

There was no relationship between watershed area or stream order and $\delta^{18}\text{O}$ variability for the four watersheds. The rsd values for $\delta^{18}\text{O}$ ranged only between 4.8 - 7.1% and the average annual value for the study period only ranged between -5.0 and -5.4 per mil. The rsd values observed for ^3H and $\delta^{18}\text{O}$ for the limited set of shallow ground analyses were within the range of the observed stream base flow. The shallow ground water data strongly suggest that most of the seasonal variability inherent within the isotopic composition of rainfall is removed or homogenized by mixing processes within the shallow subsurface and this process likely occurs in all watersheds with developed soil profiles (DeWalle et al., 1997 and Wenner et al., 1991). Both the tritium and stable oxygen isotope results indicate that rainfall is processed (i.e. stored and transmitted through the subsurface to stream channels) in a similar manner through Piedmont Province watersheds once the basin area exceeds just a few square kilometers. The movement of ground water through larger basins does not necessarily create greater isotopic homogenization. There exists a small measure of isotopic variability associated with all of the basins that exceeds analytical uncertainty and therefore isotopic homogenization (removal of seasonal or annual differences from ground water recharge) is not complete on any basin scale.

Major Ion Geochemical Variability and Basin Scale:

The highest solute loads were associated with the smallest basin (Indian Creek - first order tributary) where the average alkalinity concentration (35.9 mg/L) and specific conductance (92.6 $\mu\text{S}/\text{cm}$) in base flow were respectively 40% and 26% greater than within Pole Branch

Creek base flow which was characterized by the lowest base flow solute concentrations. The higher solute concentrations may well be related to impacts of the horse pastures located on the small Indian Creek watershed and the relatively low solute concentrations measured in Pole Branch Creek base flow may be related to the relatively undisturbed nature of this watershed.

The results of the previously discussed F-tests indicate that the chemical composition of base flow within the Indian Creek (first-order tributary) is significantly more variable with respect to a number of parameters (magnesium, alkalinity, specific conductance) than both shallow ground water (in which the total solute concentrations were relatively very low) and base flow from several of the larger watersheds. In short, although rainfall may be processed in more or less the same manner independent of watershed area, base flow within the smallest of the watersheds was apparently slightly more vulnerable to contamination from activities that were occurring on the land surface than the larger watersheds. Interestingly, the Indian Creek 2nd order basin (watershed area = 12.7 km²) was characterized by lower solute concentrations and less geochemical variability than its feeder stream. Other than the smallest basin having the highest dissolved solute concentrations and the most geochemical variability, there are few (if any) other generalizations that can be made regarding the relationship between solute concentrations and basin scale. There is a degree of randomness to this in that if a larger basin was the site of some contaminating land-use activity, it would have possibly been characterized by the highest solute concentrations.

Mass balance or end-member mixing models (e.g. Burns et al., 2001) which attempt to quantify the percentage of ground water and storm runoff most often assume that the chemical composition of the ground water component (base flow) is constant. The results of this present study indicate that this is a tenuous assumption with regards to these Piedmont Province

watersheds. The first problem is that the chemistry of base flow does not at all resemble the chemistry of shallow ground water at the one site in which it was sampled. Ground water at this upslope location was chemically non-evolved and more closely resembled rainwater in terms of low pH, solute loads, and alkalinity than it did base flow. These results suggest that it is *not* likely that the ground water at any one single location or depth will be totally representative of base flow within that watershed.

The second problem with assuming that base flow can be regarded as an invariant end member is that there was significant temporal variability associated with many of the major ion parameters and this variability was greater than the analytical uncertainties. For example, the analytical uncertainty associated with the alkalinity titrations was approximately 6% while the relative standard deviation for alkalinity was 10% or greater in the base flow. Similar considerations apply for most of the other ions, including magnesium which is an ion that was very precisely measured (analytical uncertainties were ~3-4%) while relative standard deviations for base flow were approximately twice as high. In that the only likely important source of magnesium is rock weathering, there is not one source of magnesium that produces the identical magnesium concentration in base flow throughout the year. Similar considerations apply for alkalinity which is also derived through rock weathering. There were apparently few seasonal trends with respect to base flow chemical variation other than the previously described increased bicarbonate concentrations during the dry months. This trend, however, was not clearly apparent within all the base flow and no inferences can be made with respect to basin scale.

Strontium Isotope Variability and Basin Scale:

The principal new findings of this investigation involved strontium isotope systematics within the Middle Oconee River basin and their hydrological implications for the Georgia Piedmont Province. There are two features related to $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that may prove useful in

future watershed studies in this region. First, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios apparently provide a unique geochemical signature or fingerprint of a given Piedmont Province basin (on all scales studied in this investigation). No other geochemical or isotopic parameter provides any similar unique results. The second feature is that, unlike most all other parameters, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain temporally invariant within a given basin and appear to be independent of discharge, contamination inputs, and other seasonal effects. This was the case on all basin scales. In another similar watershed study (e.g. Åberg et al., 1989), strontium isotope ratios were not time-invariant and varied inversely with discharge.

Strontium isotopes above all are a signature of the types of minerals that weather within an aquifer or watershed (Bullen and Kendall, 1998 and Négrel and Lachassagne, 2000). The rocks in this watershed were similar; however, variable percentages of amphibolite (see Figure 2), mica schist, and potassium feldspar unique to a given watershed have produced $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in base flow that are significantly different from one another to the fifth decimal place. The two closest and most geologically similar watersheds within the Indian Creek sub-basin were characterized by the two most similar sets of strontium isotope ratios (Figure 13). It should also be noted that the range of strontium ion concentrations (typically between 20-25 ppb) were quite similar in base flow within all four of watersheds, likely as a result of similar weathering processes effecting very similar minerals (Figure 14).

Shallow ground water was characterized by much lower strontium concentrations as well as very low alkalinity values (i.e. < 5 mg/L) and pH (< 6.0). The shallow ground water retained the relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios characteristic of rainfall in the study area. Rock weathering has produced little strontium in shallow ground water and perhaps the major source of strontium in these shallow waters is ion exchange. It can be inferred from the characteristically higher Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that rock weathering, rather than ion exchange from shallow

soil horizons, is the dominant source of strontium in base flow. Miller et al. (1993) also determined rock weathering, rather than ion exchange accounted for the dominant source of strontium to river water in a high-elevation watershed in upstate New York.

The seasonal variations in water flux which manifest themselves in variable discharge and in possibly some geochemical variability (see previous discussion) do not appreciably affect the strontium isotope ratio within base flow. In that rainfall was characterized by relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, there can not be an appreciable component of seasonal rainfall within the base flow. This conclusion is consistent with the very low concentrations of Sr in rainfall (< 4 ppb; Table 4) and the previously discussed environmental isotope ($\delta^{18}\text{O}$ and ^3H) results. Whatever the mineral sources of strontium are within a given watershed, the weathering reactions are apparently independent of the variable seasonal hydrological flux that occurs. Douglas et al. (2002) also observed that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were seasonally constant within the Connecticut River watershed even though there was a significant atmospheric source of strontium within these waters.

One of the interesting trends related to $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is that they tend to increase with increasing basin scale although total strontium concentrations remain more or less constant (Figure 14). Bullen and Kendall (1988) noted an inverse relationship between basin scale in several basins. The trends that were observed cannot be explained solely in terms of simple mixing in that the strontium concentrations and their related $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values do not fall on a mixing line (Figure 15) (Faure, 1986). Furthermore, if the strontium isotope ratios were solely controlled by the mixing of water from upstream tributaries than it would not be possible to mix waters with a lower ratio (e.g. Pole Branch Creek and Indian Creek) to produce a downstream sample that is characterized by a higher ratio (Middle Oconee River near Arcade; Figure 13).

It is uncertain as to why ratios apparently increase with stream order and watershed area; however, it is possible that as basin size increases the base flow will incorporate weathering products from a larger set of minerals. This set may include some of the more chemically resistant minerals such as K-feldspar that has a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the trace substitution of the ^{87}Rb which is the radiogenic parent of ^{87}Sr . The same considerations hold true with respect to muscovite which has an even higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than K-feldspar (Bullen and Kendall (1998); however, is less chemically resistant to weathering. Interestingly, Bullen and Kendall (1988) noted an *inverse* relationship between basin scale and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Sleepers River Research Watershed in Vermont and attributed this to decreasing contributions from the vadose zone.

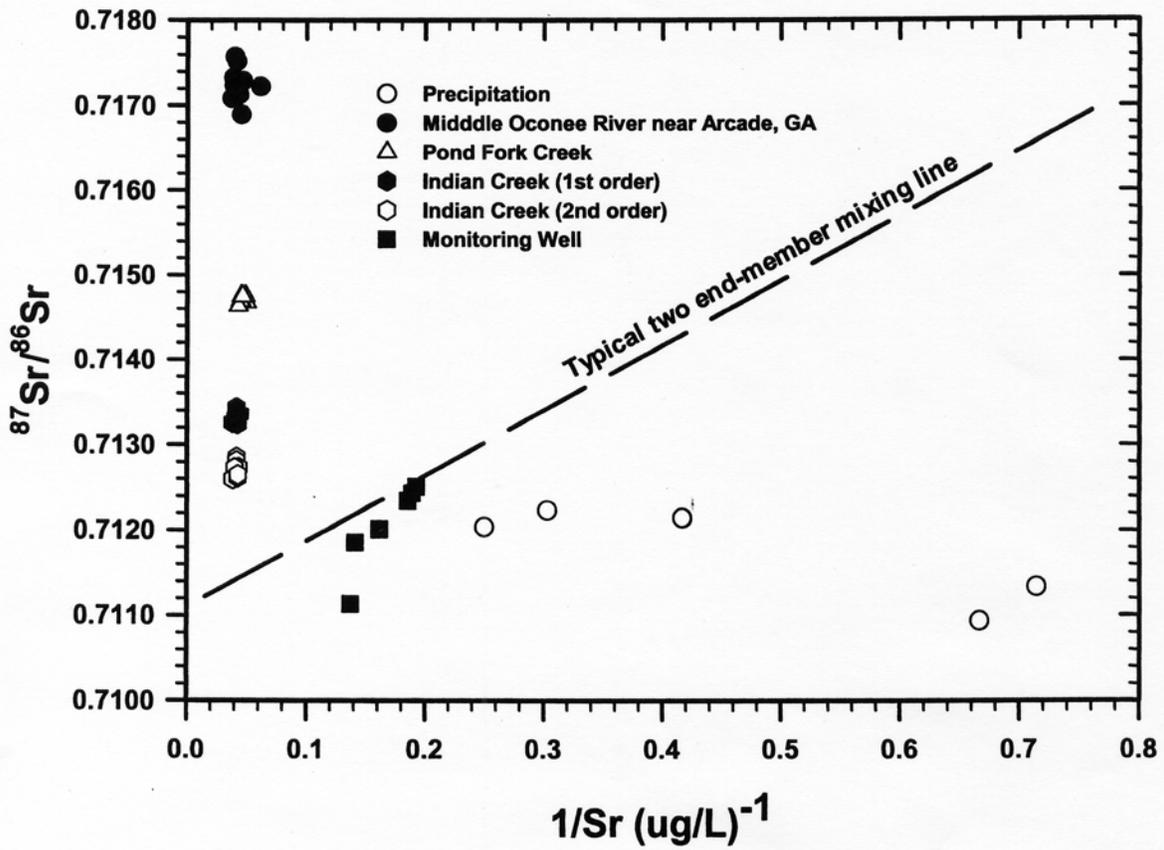


Figure 15. Relationship between strontium isotope ratios and strontium ion concentrations in base flow within the Middle Oconee River basin

Possible Uses for Strontium Isotope Systematics in Regional Watershed Studies:

The two findings of this research related to Sr isotope ratios - that they are temporally invariant in base flow at a given location and they are distinctly different between different watersheds - have important implications for how they can be used in future hydrological studies of Piedmont Province watersheds. Strontium isotopes ratios are the most constant and accurately measured of all of the water chemistry parameters that are available to the hydrologist. For purposes of illustration, the relative standard deviations with respect to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are 250-500 times lower than alkalinity variation in base flow within the Middle Oconee River basin. This would be true for all of the major ion and environmental isotopic parameters as well. Therefore, any type of study that seeks to analyze the many problems that involve mixing dynamics should seek to utilize Sr isotope ratios in addition to other parameters.

One such problem involves end-member mixing from different horizons in the soil and subsurface (Hooper et al., 1990 and Christophersen et al., 1990). It was shown in this study that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in shallow ground water are significantly lighter than base flow and though not nearly as temporally invariant as the base flow samples, they are still relatively constant. This is likely as the result of an equilibrium that occurs between soil waters, shallow ground water and the exchange population of Sr ions present on the soil matrix. Therefore, their average composition can be possibly considered as an end-member in various mixing scenarios. Strontium isotopic ratios can provide a critical tool for studies of the mixing dynamics between tributaries within a surface water network in that each sub-watershed would likely bear its own strontium isotopic signature. Similar uses can be made in calculating water balances to lakes and reservoirs. Strontium isotope ratios may provide an adequate tool for differentiating and quantifying the amount of water that flows into a given downstream stretch of river from various upstream tributaries as well as base flow emanating from the down stream basin of interest.

Strontium isotope ratios can certainly be used to provide an excellent tracer in storm-water mixing studies in that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of rainfall was found to be considerably lighter than that of base flow within this Piedmont Province study area.

SUMMARY AND CONCLUSIONS

Major ion geochemistry, environmental isotope (^3H and $\delta^{18}\text{O}$), and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotope ratio variation was analyzed within rainfall, shallow ground water and base flow in the 860 km² Middle Oconee River basin near Arcade in Jackson County, Georgia. Water samples were acquired on an approximate monthly basis during the period between March, 2003 - March, 2004. The most general objective was to analyze the chemical and isotopic variability of base flow within the study area and relate these variations to their hydrological controls. These results likely represent the first systematic utilization and interpretation of strontium isotopic variation for Piedmont Province watersheds in Georgia. The major conclusions from this study are as follows:

1) The rate of base flow varies systematically during the course of the year within the Middle Oconee River and other Piedmont Province watersheds. The rate of base flow declines by a factor of approximately 2-3 between April and October when water deficit conditions exist.

2) Environmental tritium concentrations within the shallow ground water (average = 16 T.U.) were approximately twice as great as recent rainfall (5-10 T.U.). There is no doubt that a bomb component (i.e. water recharged during the period of atmospheric testing during the 1960's) is present within the shallow ground water. ^3H concentrations within base flow vary between 7-15 T.U. which as a range is higher than recent rainfall but lower than the ground water. This indicates that there is also a bomb component of recharge present within the base flow and possibly also a pre-bomb component (with no-tritium) as well. There were different

ranges of tritium concentrations observed in each of the four watersheds; however, there was no consistent nor readily interpretable relationship between tritium concentrations and basin scale.

3) Stable oxygen isotope ratios ($\delta^{18}\text{O}$) varied between ± 5.4 and -5.0 per mil (relative to SMOW) which is very similar to the average yearly rainfall within the region. The variations observed during the sampling period were slightly greater than analytical error; however, $\delta^{18}\text{O}$ ratios did not become appreciably lighter in stream base flow or shallow ground water during the winter months indicating there is not a significantly large seasonal precipitation input to the ground water that comprises base flow.

4) Base flow within the Middle Oconee River watershed is not chemically constant during the course of the year. The variations that were observed (rsd values between ± 5 - 30%) for most of the major ion parameters are greater than analytical errors. With the exception of alkalinity concentrations, the variation is not seasonal or related to the rate of base flow discharge. The greatest variations were observed in the smallest watershed (Indian Creek - 1st order tributary) which was only 3.9 km^2 . There were few differences with respect to major ion variation at a watershed scale of greater than $\pm 10 \text{ km}^2$. The hydrological significance of this major ion variability is not clear; however, it may be partially related to influx of contaminants (from horse pastures, small water treatment facilities, and leaky septic tanks) and partially related to differential inputs of water from variable source areas within a given basin. The important conclusion from this is that base flow within these watersheds can *not* be considered a chemically constant, temporally-invariant, body of water. The variation is small but significant.

5) The chemistry of the shallow ground water at depths of ± 8 meters below the water table at an upslope well-site much more closely resembled that of rainfall (e.g. specific conductance $< 32 \text{ uS/cm}$, pH < 5.3 , alkalinity $< 6 \text{ mg/L}$) than base flow. This implies that base flow is derived from deeper ground water bodies and a great deal of chemical weathering occurs

as ground water flow downslope to the stream channel. It also indicates that ground water from any given monitoring well or even a set of monitoring wells may not produce water that resembles the chemical composition of base flow.

6) Strontium ion concentrations in these waters are relatively low (typically <25 ppb) and do not vary greatly from watershed to watershed. Concentrations are approximately four times higher in base flow than in rainfall or shallow ground water indicating the predominant source of strontium in base flow is mineral weathering rather than direct atmospheric input or ion exchange reactions in the shallow subsurface.

7) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are significantly different in base flow from each of the four watersheds and the base flow was significantly more radiogenic (higher ratios) than rainfall and shallow ground water. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were virtually temporally invariant within a given stream and therefore those hydrological processes that affect changes in base flow discharge rates and major ion chemistry do not affect the isotopic composition of strontium in these streams. The strontium isotope ratio became more radiogenic with increasing basin area perhaps as the result of increased weathering contributions of muscovite and potassium feldspar in the larger watersheds.

8) The unique strontium isotopic signature of a given watershed along with the temporal constancy of these $^{87}\text{Sr}/^{86}\text{Sr}$ ratios make for an almost ideal tracer. Therefore, strontium isotope ratios can be used to quantify or assess the mixing of ground water and storm runoff, the infiltration of vadose zone water, the contribution of ground water to stream runoff, lakes and reservoirs and other hydrological processes that occur within the Piedmont Province.

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Appendix 1

Precipitation Record (in inches)

From the USDA- ARS collection site at Watkinsville; Oconee Co., GA. Georgia Automated Environmental Network: <http://www.griffin.peachnet.edu>

Day	2003					2004							
	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar
1	0.08		0.02		4.82								
2			0.32			0.01	0.5					0.66	
3				0.83		0.26				0.07			
4	0.03			0.06		0.64	0.09		0.02	0.57	0.38	0.01	
5	0.86	0.11	1.96		1.82	0.01			0.44			1.15	
6	1.17	0.05	1.26	0.47		0.01		0.06	0.01				0.13
7	0.11	0.55	0.38	1.75	0.01	0.21		0.01		0.01	0.04		
8		0.23	0.34					0.17			0.27		
9		0.07				0.28		0.01	0.04				
10		0.53			1.34				0.01	0.95			
11		0.01	0.09	0.09	0.15	0.23						0.15	
12				0.02		0.62						1.29	
13				0.95	1.49					0.25			
14	0.02		0.53	0.52						0.22		0.54	
15	0.55		0.32									0.47	
16				0.17		0.14		0.03					0.04
17	0.93	0.39	0.55	0.08					0.03	0.15	0.1		
18	0.12		0.01	0.06					0.91	0.02	0.3		
19	1.14		0.02						1.29				
20	0.58		0.24		0.02								0.09
21	0.01	0.33	2.45		0.14		0.01						0.07
22					0.46		1.42						
23					0.98		0.01			0.31		0.22	
24		0.02			0.01					0.01		0.31	
25		0.57							0.21		1.65	0.12	
26			0.02			0.07		1.43	0.13			0.29	
27	0.7			0.03	0.06		1.3		0.39		0.19	0.01	
28				0.37									
29													
30	0.15			0.24	0.02								0.59
31					1.24					0.03			0.05
Total	6.45	2.86	8.51	5.64	12.63	2.41	3.33	1.71	3.48	2.59	2.93	5.22	0.97

APPENDIX 2

Discharge Record for the Middle Oconee River near Arcade, GA. (USGS Gage No. 022174745)

Study Period: March, 2003 - March 2004 (Data Source: <http://ga.waterdata.usgs.gov/>)

All Values are in Cubic Feet per Second (cfs) and Represent Daily Maximum Values

Day	March	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar
1	2003	513	392	435	5280	1280		207	220	372	321	394	408
2		498	465	415	10800	653			209	331	311	387	398
3		478	433	389	10100	511	261		211	313	317	674	415
4		470	405	431	2530	511	350	202	236	412	315	564	415
5		524	374	448	1930	902	285	202	261	429	389	419	392
6		527	419	405	1300	635	241	202	524	387	480	2070	419
7		662	441	383	1050	621	226	211	433	329		2210	398
8		589	480	387	874	473	220	227	305	309	307	955	403
9		545	493	1030	677	623	219	245	266	295	369	656	363
10		748	511	800	767	626	211	259	245	754	376	545	369
11		964	579	615	942	629	202	239	236	955	333	493	361
12		716	556	524	683	532	201	234	238	543	307	1419	335
13		564	540	1400	783	527	191		236	415	301	1350	329
14		511	490	1719	2370	463	167	196	226	933	303	833	329
15		478	480	1729	1690	408	217	199	220	850	295	659	331
16		450	556	1060	823	356	209	178	212	508	283	584	354
17	793	443	556	3300	716	483	184	178	295	470	274	521	356
18	958	470	521	3560	581	396	173	184	348	343	358	480	323
19	767	463	559	2920	513	325	167	184	2380	283	358	468	319
20	7070	426	559	1690	475	301	166	178	2290	277	297	429	311
21	7510	475	562	1040	463	354	159	175	745	261	287	426	350
22	3240	939	567	757	803	309	490	170	495	346	274	422	346
23	1330	553	567	623	823	283	1440	167	405	352	268	495	301
24	1040	422	567	556	671	268	641	167	394	595	261	426	293
25	877	970	570	535	488	263	313	173	405	564	1570	422	291
26	777	1040	589	465	426	263	246	350	350	405	1880	495	291
27	698	609	598	438	398	253	261	671	343	438	1140	519	291
28	641	495	598	578	387	238	448	424	653	348	695	498	293
29	612	438	545	584	363	238	350	274	612	329	543	441	289
30	600	415	503	478	343		232	241	419	363	473		367
31	595		465		490			224		363	422		394
Total	29,511	17,395	15,940	29,694	50,539	13,724	8,470	6,561	14,412	13,872	14,107	20,254	10,834

APPENDIX 3
Environmental Tritium Concentrations in Tritium Units (T.U.)
Analyses are from the Environmental Isotope Laboratory, University of Waterloo

Rainfall

	Tritium (T.U.)	Std. Dev.	Weighted Period	Repeats (T.U.)	Repeats (T.U.)
	6.9	0.8	Weighted rainfall from March to December, 2003		
	7.5	0.7	Weighted rainfall from January to March, 2004	7.2	7.8
Average	7.2				
Std. Dev.	0.4				
Rel. Std. Dev. (%)	5.9				
Range	6.9-7.5				
Number	2				

Middle Oconee River near Arcade, Ga.

Date	Tritium (T.U.)	Std. Dev.	Repeats (T.U.)	Repeats (T.U.)
4/24/2003	8.6	0.9		
5/28/2003	7.9	0.9		
6/25/2003	7.2	0.7		
8/19/2003	10.6	0.9		
10/23/2003	7.9	0.8	7.1	8.7
12/2/2003	14.0	1.2		
1/2/2004	9.3	0.9		
3/2/2004	7.3	0.8		
Average	9.1			
Std. Dev.	2.3			
Rel. Std. Dev. (%)	25.0			
Range	7.3 - 14.0			
Number	8			

Note: 1 T.U. = 1 tritium atom in 1 E18 atoms of hydrogen in water

APPENDIX 3

Environmental Tritium Concentrations in Tritium Units (T.U.)
Analyses are from the Environmental Isotope Laboratory, University of Waterloo
Indian Creek (2nd order)

Date	Tritium (T.U.)	Std. Dev.
12/2/2003	11.1	1.0
3/2/2004	10.5	0.9
Average	10.8	
Std. Dev.	0.4	
Rel. Std. Dev. (%)	3.7	
Range	10.5-11.1	
Number	2	

Pole Branch Creek

Date	Tritium (T.U.)	Std. Dev.
3/27/2003	9.0	0.9
5/28/2003	10.0	1.0
8/19/2003	9.7	0.9
10/23/2003	10.0	0.9
12/2/2003	10.8	1.0
3/2/2004	11.1	1.0
Average	10.1	
Std. Dev.	0.8	
Rel. Std. Dev. (%)	7.5	
Range	9.0-11.1	
Number	6	

APPENDIX 3
Environmental Tritium Concentrations in Tritium Units (T.U.)
Analyses are from the Environmental Isotope Laboratory, University of Waterloo
Indian Creek (1st order)

Date	Tritium (T.U.)	Std. Dev.	Repeats (T.U.)	Repeats (T.U.)
5/28/2003	7.6	0.8		
8/19/2003	11.1	1.0	10.5	11.7
10/23/2003	16.6	1.4		
12/2/2003	10.5	0.9		
1/2/2004	11.8	1.0		
3/2/2004	11.1	1.0	11.7	10.5
Average	11.5			
Std. Dev.	2.9			
Rel. Std. Dev. (%)	25.5			
Range	7.6-16.6			
Number	6			

Shallow Ground Water Monitoring Well				
Date	TU	Std Dev	Repeats	Repeats
8/19/2003	20.5	1.5		
10/23/2003	17.0	1.4		
12/2/2003	15.5	1.3		
1/2/2004	12.2	1.0		
3/2/2004	14.0	1.1		
Average	15.8			
Std. Dev.	3.2			
Rel. Std. Dev. (%)	19.9			
Range	12.2 - 20.5			
Number	5			

APPENDIX 4

**Stable Oxygen Isotope Ratios (in per mil relative to SMOW)
Analyses made by Geochron Laboratories**

Rainfall (collected in Decatur, GA)				Middle Oconee River near Arcade, Ga.		Indian Creek (2nd order)		
Collection Date	Inches Rain	Del O-18 per mil	Repeat	Collection Date	Del O-18 per mil	Collection Date	Del O-18 per mil	Repeat
6/3/2003	0.5	-4.8		3/27/2003	-6.0	4/24/2003	-4.6	
6/17/2003	3.3	-5.9		4/24/2003	-5.6	5/28/2003	-5.4	
7/1/2003	3.4	-4.4		5/28/2003	-5.3	6/25/2003	-4.4	
7/23/2003	1.3	-4.5		6/25/2003	-5.1	7/20/2003	-5.2	
8/7/2023	1.5	-4.4		7/20/2003	-5.3	8/19/2003	-5.3	
9/22/2003	1.8	-4.5		8/19/2003	-5.6	9/20/2003	-5.0	
10/17/2003	0.40	-1.8		9/20/2003	-5.4	12/2/2003	-5.1	
10/26/2003	1.70	-4.7		10/23/2003	-5.0	3/2/2004	-5.3	-5.3
11/5/2003	1.30	-4.4		12/2/2003	-5.8			
11/18/2003	2.80	-7.6		1/2/2004	-5.1			
1/9/2004	1.50	-4.3		3/2/2004	-5.4			
1/29/2004	2.50	-5.8	-6.1					
2/11/2004	1.60	-8.1						
Unweighted Average			-5.0	Average	-5.4	Average	-5.0	
Unweighted Std. Dev.			1.6	Std. Dev.	0.3	Std. Dev.	0.4	
Rel. Std. Dev. (%) Number			31.8 13	Rel. Std. Dev. (%) Number	5.7% 11	Rel. Std. Dev. (%) Number	7.1% 8	

APPENDIX 4
Stable Oxygen Isotope Ratios (in per mil relative to SMOW)
Analyses made by Geochron Laboratories

Pond Fork Creek				Indian Creek (1st order)		Shallow Ground Water Monitoring Well	
Collection Date	Del O-18 per mil	Repeat	Repeat	Collection Date	Del O-18 per mil	Collection Date	Del O-18 per mil
3/27/2003	-5.2			4/24/2003	-5.4	8/19/2003	-5.7
4/24/2003	-5.0			5/28/2003	-5.4	10/23/2003	-5.4
5/28/2003	-5.2			6/25/2003	-4.9	12/2/2003	-5.5
6/25/2003	-5.5	-5.2	-5.9	7/20/2003	-4.8	2/1/2004	-5.5
		-5.7	-5.4	9/20/2003	-5.3	3/2/2004	-6.1
7/20/2003	-5.2			10/23/2003	-5.3		
8/19/2003	-4.9			12/2/2003	-4.8		
12/2/2003	-5.1			2/1/2004	-5.1		
3/2/2004	-5.7			3/2/2004	-5.1		
Average	-5.2			Average	-5.1	Average	-5.6
Std. Dev.	0.3			Std. Dev.	0.3	Std. Dev.	0.3
Rel. Std. Dev. (%)	7.1			Rel. Std. Dev. (%)	5.0	Rel. Std. Dev. (%)	5.0
Number	8			Number	9	Number	5

APPENDIX 5
Summary of Major Ion Geochemical Data
Middle Oconee River near Arcade, Georgia

Date	Temp. (oC)	Specific Conductance (uS/cm)	pH	Alkalinity (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
3/27/2003	18.4	70.0	6.00	29.3	6.7	1.8	5.4	2.4	4.8	5.2
4/24/2003	15.4	78.9	6.69	24.4	6.6	1.9	5.7	2.1	2.1	5.8
5/28/2003	18.1	86.4	6.39	24.4	8.7	2.0	5.7	1.9	8.7	5.1
6/25/2003	24.0	78.3	6.69	28.4	10.4	1.8	5.1	2.4	4.9	4.8
7/20/2003	26.1	80.4	6.83	26.4	9.5	1.8	5.2	2.5	4.7	5.0
8/19/2003	25.3	85.3	6.69	28.5	8.2	2.0	5.9	2.5	4.5	7.4
9/20/2003	22.9	88.6	6.89	33.3	8.2	2.0	6.6	2.3	5.6	7.9
10/23/2003	17.1	76.4	7.08	32.5	14.8	1.8	7.0	2.6	5.3	7.9
12/2/2003	9.1	84.4	6.86	28.1	11.1	1.8	6.2	2.3	5.6	10.4
1/2/2004	10.6	78.3	6.60	26.0	4.4	1.7	5.7	1.7	4.3	10.3
2/1/2004	6.7	92.3	7.06	26.0	4.1	2.0	6.8	1.8	8.4	11.4
3/2/2004	14.4	83.6	6.67	25.2	4.3	1.8	6.4	1.7	6.2	11.0
Low	6.7	70.0	6.00	24.4	4.1	1.8	5.1	1.7	2.1	4.8
High	24.0	92.3	7.08	33.3	14.8	2.0	6.8	2.6	8.7	11.0
Average	17.3	81.9	6.70	27.7	8.1	1.9	6.0	2.2	5.4	7.7
Std. Dev.	6.4	6.1	0.29	2.9	3.2	0.1	0.6	0.3	1.8	2.5
Rel. Std. Dev. (%)	37.1	7.4	4.4	10.5	39.1	5.7	10.4	15.1	32.8	33.2
Number	12	12	12	12	12	12	12	12	12	12

Appendix 5
Summary of Major Ion Geochemical Data
Indian Creek (2nd order stream)

Date	Temper. (oC)	Specific Conductance (uS/cm)	pH	Alkalinity (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
4/24/2003	15.2	76.6	6.51	30.9	9.0	1.9	5.4	1.9	2.1	5.6
5/28/2003	17.1	80.1	6.38	32.1	7.0	1.9	5.2	2.2	2.5	5.5
6/25/2003	21.7	81.5	6.61	33.3	6.6	1.9	5.4	2.1	1.9	5.5
7/20/2003	27.2	77.6	6.52	30.1	8.8	1.8	5.2	2.7	1.9	5.6
8/19/2003	26.0	84.3	6.67	26.0	8.2	2.0	5.5	2.1	1.3	7.1
9/20/2003	22.6	81.3	6.98	34.6	8.6	2.0	5.6	2.0	2.6	6.2
10/23/2003	18.1	73.4	6.96	36.6	9.2	1.9	6.1	2.2	1.2	8.1
12/2/2003	10.9	59.5	7.01	30.9	9.7	1.8	5.8	2.0	2.2	10.2
1/2/2004	10.8	82.5	6.90	29.3	4.3	1.8	5.8	1.4	2.2	10.7
2/1/2004	6.4	84.8	6.82	26.8	4.0	1.8	5.8	1.5	2.7	11.6
3/2/2004	14.7	80.4	6.80	26.0	3.9	1.8	6.5	1.2	2.4	10.7
Low	6.4	59.5	6.38	26.0	3.9	1.8	5.2	1.2	1.2	5.5
High	27.2	84.8	7.01	36.6	9.0	2.0	6.1	2.2	2.6	11.6
Average	17.3	78.4	6.74	30.6	7.2	1.9	5.7	1.9	2.1	7.9
Std. Dev.	6.6	7.1	0.22	3.5	2.2	0.1	0.4	0.4	0.5	2.4
Rel. Std. Dev. (%)	38.0	9.1	3.2	11.3	30.7	4.2	6.9	21.9	23.0	31.0
Number	11	11	11	11	11	11	11	11	11	11

APPENDIX 5
Summary of Major Ion Geochemical Data
Pond Fork Creek

Date	Temper. (oC)	Specific Conductance (uS/cm)	pH	Alkalinity (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
3/27/2003	19.1	68.6	6.36	23.6	6.0	1.9	4.3	1.8	2.7	4.8
4/24/2003	12.7	76.9	6.83	26.8	6.5	1.9	4.6	2.1	2.4	4.9
5/28/2003	18.7	72.5	6.82	28.5	9.2	1.8	4.5	2.4	2.1	5.1
6/25/2003	23.6	75.1	6.83	22.7	9.2	1.9	4.6	2.3	2.0	5.1
7/20/2003	27	76.4	6.92	26.8	7.1	1.8	4.8	2.4	1.8	5.3
8/19/2003	23.6	77.1	7.06	30.5	7.4	1.9	5.1	2.3	3.8	7.0
9/20/2003	23.6	76.4	6.92	29.7	7.2	1.8	5.4	2.3	1.2	7.5
10/23/2003	16.9	66.2	6.91	30.1	12.8	1.7	5.3	2.2	1.5	9.8
12/2/2003	9.9	78.3	7.15	26.0	4.2	1.7	6.0	2.0	2.1	10.1
1/2/2004	8.7	78.1	6.55	23.6	4.4	1.7	5.2	1.5	2.0	9.7
2/1/2004	8.8	72.2	6.89	25.6	3.9	1.8	4.5	1.2	2.1	9.1
3/2/2004	17.4	73.5	6.61	24.4	3.9	1.6	4.7	1.1	2.0	9.9
Low	8.7	66.2	6.36	22.7	3.9	1.6	4.3	1.1	1.8	4.8
High	23.6	78.3	7.06	30.5	12.8	1.9	6.0	2.1	3.8	10.1
Average	17.5	74.3	6.82	26.5	6.8	1.8	4.9	2.0	2.1	7.3
Std. Dev.	6.3	3.8	0.22	2.7	2.7	0.1	0.5	0.5	0.6	2.3
Rel. Std. Dev. (%)	36.1	5.1	3.2	10.2	39.1	5.6	10.0	23.6	29.9	30.7
Number	12	12	12	12	12	12	12	12	12	12

APPENDIX 5
Summary of Major Ion Geochemical Data
Indian Creek (1st order)

Date	Temper. (oC)	Specific Conductance (uS/cm)	pH	Alkalinity (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
4/24/2003	15.1	86.9	6.53	30.5	7.9	1.6	7.7	2.0	2.1	7.5
5/28/2003	16.0	112.2	5.99	47.2	9.8	NA	2.9	2.5	3.7	5.1
6/25/2003	21.2	93.2	6.58	34.6	8.0	1.6	7.7	2.3	2.0	7.4
7/20/2003	24.8	96.6	6.61	36.6	8.4	1.8	8.3	2.6	2.0	7.9
8/19/2003	24.2	92.9	7.06	32.5	8.0	1.7	7.4	2.1	1.5	9.4
9/20/2003	21.7	87.3	6.63	32.5	5.2	1.7	7.2	2.0	1.3	9.7
10/23/2003	16.9	84.5	6.67	39.9	13.8	1.4	9.4	2.5	1.1	11.6
12/2/2003	11.4	74.8	6.68	37.8	12.9	1.8	9.7	2.3	2.2	14.7
1/2/2004	12.2	98.1	6.45	35.0	3.9	1.4	8.4	1.7	2.1	14.4
2/1/2004	7.6	102.0	6.50	37.0	3.7	1.4	8.7	1.8	2.9	14.7
3/2/2004	15.1	89.7	6.50	31.3	3.6	1.4	4.1	1.5	2.6	12.8
Low	7.6	86.9	6.53	30.5	3.6	1.4	4.1	1.5	1.1	5.1
High	24.2	112.2	7.06	47.2	13.8	1.8	9.4	2.6	3.7	14.4
Average	16.9	92.6	6.56	35.9	7.7	1.6	7.4	2.1	2.1	10.5
Std. Dev.	5.5	9.9	0.25	4.7	3.5	0.2	2.1	0.4	0.7	3.4
Rel. Std. Dev. (%)	32.5	10.6	3.8	13.2	45.2	10.7	28.4	16.9	34.6	32.3
Number	11	11	11	11	11	11	11	11	11	11

APPENDIX 5
Summary of Major Ion Geochemical Data
Shallow Monitoring Well

Date	Temper. (oC)	Specific Conductance (uS/cm)	pH	Alkalinity (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
8/19/2003	18.1	20.4	5.17	3.2	1.2	0.5	1.1	2.1	0.9	2.1
9/20/2003	19.5	32.2	5.25	6.1	1.7	0.5	2.0	1.4	0.8	4.3
10/23/2003	18.7	16.7	5.29	4.0	2.4	0.5	1.1	0.6	0.6	3.1
12/2/2003	15.4	21.1	5.18	5.4	1.0	0.5	1.1	0.5	0.8	3.3
1/2/2004	16.3	21.3	4.89	3.9	0.6	0.4	1.2	0.6	0.5	3.7
2/1/2004	15.2	15.2	5.20	2.4	0.6	0.5	1.1	1.7	0.5	4.0
3/2/2004	17.5	20.4	5.23	2.7	0.5	0.5	1.0	0.2	0.2	0.0
Low	16.3	15.2	4.89	2.7	0.5	0.4	1.0	0.2	0.2	0.0
High	19.5	32.2	5.29	6.1	2.4	0.5	2.0	2.1	0.9	4.3
Average	17.2	21.0	5.17	4.0	1.1	0.5	1.2	1.0	0.6	2.9
Std. Dev.	1.7	5.5	0.13	1.4	0.7	0.04	0.3	0.7	0.2	1.5
Rel. Std. Dev. (%)	9.6	25.9	2.5	34.6	61.0	7.8	28.1	70.5	38.5	50.5
Number	7	7	7	7	7	7	7	7	7	7

APPENDIX 6
Strontium Concentrations and Isotope Ratios
Strontium Concentrations and 87/86 Isotope Ratios Analyzed at the Department of Geology, University of North Carolina

Dates	Rainfall				Middle Oconee River near Arcade, Ga.			
	Rainfall Collected (cms)	Strontium Conc. (ppb)	Strontium 87/86 Ratio	Percent Std. Error	Date	Sr Conc. (ppb)	Strontium 87/86 Ratio	Percent Std. Error
6/03 - 6/31/03	11.4	1.4	0.711336	0.0014	3/27/2003	1.4	0.716981	0.0006
7/1/03 - 9/22/03	19.3	2.4	0.712139	0.0024	4/24/2003	16.3	0.717223	0.0006
9/28/03- 10/26/03	11.2	4.0	0.712033	0.0040	5/28/2003	25.1	0.717572	0.0007
10/26/03 - 11/18/03	17.3	3.3	0.712249	0.0033	6/25/2003	24.9	0.717043	0.0007
1/1/03- 3/31/03	26.4	1.5	0.710932	0.0015	7/20/2003	25.9	0.717324	0.0007
Unweighted Average		2.5	0.711738		8/19/2003	25.6	0.717233	0.0007
Unweighted Std. Dev.		1.1	0.000574		10/23/2003	26.9	0.717081	0.0008
Unweighted Rel. Std. Dev. (%)		44.8	0.08		12/2/2003	21.5	0.717289	0.0007
					1/2/2004	23.7	0.717264	0.0007
					2/1/2004	23.1	0.717217	0.0008
					3/2/2004	24.1	0.717157	0.0007
					AVERAGE	21.7	0.717217	
					STD. DEV.	7.3	0.000159	
					REL. STD. DEV.	33.7%	0.02%	
					NUMBER	11	11	

**APPENDIX 6
Strontium Concentrations and Isotope Ratios**

INDIAN CREEK - 2ND ORDER

Date	Strontium Conc. (ppb)	Strontium 87/86 Ratio	Percent Standard Error
4/24/2003	23.5	0.712712	0.0007
5/28/2003	24.1	0.712847	0.0007
6/25/2003	24.2	0.712807	0.0006
7/20/2003	23.2	0.712728	0.0008
9/20/2003	25.1	0.712723	0.0008
12/2/2003	26.2	0.712595	0.0009
1/2/2004	23.7	0.712617	0.0006
3/2/2004	23.5	0.712647	0.0007

**AVERAGE
STD. DEV.
REL. STD. DEV.
NUMBER**

**24.2
1.0
4.1%
8**

**0.712710
0.000088
0.01%
8**

Pond Fork Creek

Date	Strontium Conc. (ppb)	Strontium 87/86 Ratio	Percent Standard Error
3/27/2003	20.1	0.714677	0.0007
4/24/2003	20.5	0.714750	0.0006
5/28/2003	22.2	0.714701	0.0007
6/25/2003	22.4	0.714676	0.0007
7/20/2003	22.5	0.714695	0.0007
9/20/2003	23.3	0.714633	0.0008
12/2/2003	22.1	0.714693	0.0007
3/2/2004	21.6	0.714749	0.0007

**AVERAGE
STD. DEV.
REL. STD. DEV.
NUMBER**

**21.8
1.1
4.9%
8**

**0.714697
0.000039
0.01%
8**

INDIAN CREEK - 1ST ORDER

Date	Strontium Conc. (ppb)	Strontium 87/86 Ratio	Percent Standard Error
4/24/2003	23.5	0.713363	0.0008
6/25/2003	24.4	0.713330	0.0008
7/20/2003	24.0	0.713290	0.0008
8/19/2003	24.7	0.713314	0.0009
9/20/2003	24.2	0.713429	0.0008
10/23/2003	26.3	0.713257	0.0007
1/2/2004	23.5	0.713244	0.0008
2/1/2004	24.0	0.713244	0.0008
3/2/2004	22.6	0.713353	0.0007

**AVERAGE
STD. DEV.
REL. STD. DEV.
NUMBER**

**24.1
1.0
4.2%
9**

**0.713314
0.000062
0.01%
9**

Shallow Ground Water Monitoring Well

Date	Strontium Conc. (ppb)	Strontium 87/86 Ratio	Percent Standard Error
8/19/2003	6.2	0.712009	0.0007
9/20/2003	7.1	0.711854	0.0009
10/23/2003	7.3	0.711134	0.0009
1/2/2004	5.4	0.712341	0.0007
2/1/2004	5.3	0.712429	0.0007
3/2/2004	5.2	0.712507	0.0008

**AVERAGE
STD. DEV.
REL. STD. DEV.
NUMBER**

**6.1
0.9
15.4%
6**

**0.712046
0.000513
0.07%
6**

