STRONTIUM ISOTOPE RATIOS IN STREAM BASE FLOW WITHIN THE GEORGIA PIEDMONT PROVINCE

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REFERENCE: Proceedings of the 2005 Georgia Water Resource Conference, held April 25-27, 2005, at The University of Georgia, Kathryn J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Abstract. Strontium isotope ratios, strontium ion concentrations, major ion concentrations, and stream discharge were measured within the Middle Oconee River basin upstream of Arcade, Georgia during the period 2003-2004. Strontium isotope ratios ($^{87}Sr/^{86}Sr$) in stream base flow were between 0.7126 and 0.7172, considerably higher than rainfall (0.7117) and shallow ground water (0.7120). This indicates that Sr and by inference other weathering products in base flow are derived principally from weathering, rather than ion exchange in the shallow soil zone. Unlike all other parameters, strontium isotope ratios were temporally invariant within a given watershed, independent of seasonal variations with respect to base flow discharge. Strontium isotope ratios were significantly different in all four watersheds and therefore provide the best geochemical "tracer" for base flow. $^{87}Sr/^{86}Sr$ ratios increased as a function of basin area, independent of Sr ion concentrations, probably as the result of the increased contribution from rubidium-bearing minerals such as K-feldspar, muscovite, and biotite.

INTRODUCTION

The strontium isotope ratio ($^{87}Sr/^{86}Sr$) has been used in watershed studies to trace water pathways and define weathering reactions that control the chemistry of ground water and base flow (Bullen and Kendall, 1998). The first order control on the $^{87}Sr/^{86}Sr$ ratio in water is the degree to which rubidium (Rb-87 is the radiogenic parent of Sr-87) is present as a substitute for potassium within minerals comprising a watershed (Douglas et al., 2002). In that Piedmont Province watersheds are comprised dominantly of aluminosilicate minerals (i.e. K-feldspar, biotite, and muscovite), $^{87}Sr/^{86}Sr$ should be relatively high. One complication is that Sr derived from cation exchange reactions at shallow depths typically produces much lower $^{87}Sr/^{86}Sr$ ratios (Miller et al., 1993).

This study represents the most systematic investigation to date of strontium isotope systematics on a large basin scale (13-860 km^2) within the Georgia Piedmont Province. The principal objectives were to determine the extent of strontium isotope and strontium ion concentration variation within base flow, rainfall, and shallow ground water and how this variation relates to seasonal factors, stream discharge, major ion geochemistry, basin mineralogy, and basin area.

STUDY AREA AND METHODS

The 860 km^2 Middle Oconee River basin in Jackson County upstream of Arcade, Georgia (Figure 1) was chosen as a study area in that it is relatively undeveloped (~95% forest and pasture) and stream discharge is monitored on a continuous basis by the USGS. Shallow ground water was monitored within the regolith near the Middle Oconee River at a depth of 17 meters and rainfall samples were acquired at a location ~75 km west of the site. Stream base flow (USGS, 2004) and shallow ground water were monitored on a monthly basis during the period between March, 2003 and March, 2004. Rainfall totals were obtained near the study area from the U. S. Department of Agriculture station located at Watkinsville, Georgia, approximately 20 km southeast of the study area. Specific conductance was monitored in the field and pH and alkalinity concentrations were determined usually within 24 hours after sample collection. Tritium (^3H) and stable oxygen isotope ($\delta^{18}O$) ratios were measured on selected samples for comparative purposes.

$^{87}Sr/^{86}Sr$ ratios and Sr ion concentrations were determined at the University of North Carolina-Chapel Hill using a VG (Micromass) Sector 54 thermal ionization mass spectrometer (TIMS). These techniques produce Sr isotope ratios that have uncertainty of no more than 2 in the 5th decimal place (2standard deviations); for conciseness, we report the ratios in the 4th decimal place.

RESULTS AND DISCUSSION

The study area received 1467 mm precipitation during the study period which is 21% greater than normal and most of the excess occurred between June and July, 2003. Total discharge was likewise 37% greater than normal during the

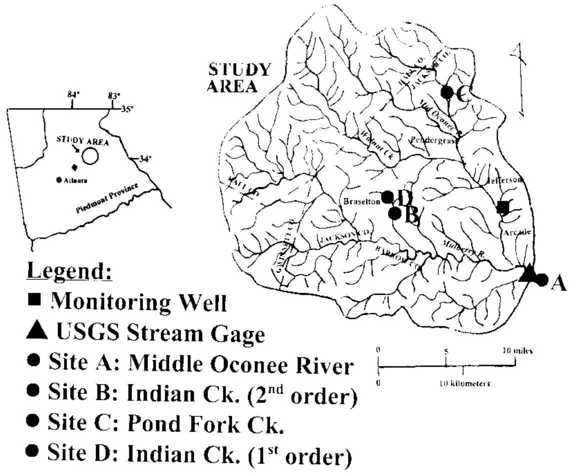

Figure 1. Middle Oconee River Basin study area showing sampling sites.

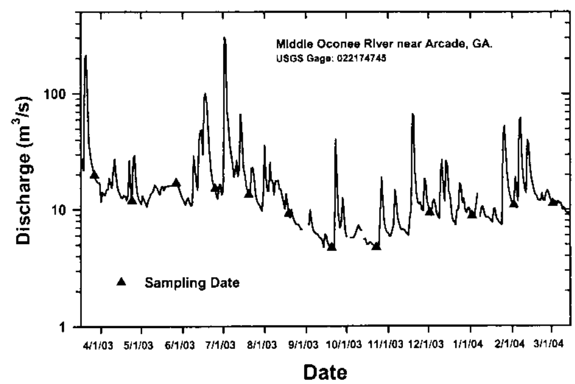

Figure 2. Stream dsicharge for the Middle Oconee River basin near Arcade GA for the study period. Sampling dates are shown in triangles. (Data from the U.S. Geological Survey, 2004.

study period. Rainfall and discharge returned to normal during the later part of the study and base flow discharge rates declined by a factor of two to three during the period between August and November, 2003 (Figure 2). This decline in base flow discharge is a defining characteristic of stream flow in the Piedmont region.

Strontium ion concentrations were relatively low in study area base flow, ranging from 16.3-26.9 µg/L (Table 1) compared to the global river average of 78 µg/L (Palmer and Edmond, 1992). Neither strontium ion concentrations nor strontium isotopic ratios varied as a function of base flow discharge during the sampling period. Strontium ion concentrations in base flow were significantly higher than in rainfall or shallow ground water (Table 1) which indicates that dominant source of Sr (and by inference other ions) in base flow is the weathering products of minerals, rather than the release of exchanged ions in shallow soil horizons.

$^{87}Sr/^{86}Sr$ ratios varied between 0.7113-0.7176 and averaged 0.7145 within base flow in the four streams (Table 1). This average is higher than the global river average (0.7119; Palmer and Edmond, 1992) and can be attributed to the dominance of Rb-bearing aluminosilicate minerals within Piedmont Province watersheds. The $^{87}Sr/^{86}Sr$ ratios in stream base flow were considerably higher than in the weighted rainfall (0.7117) and in the shallow ground water (0.7120; Table 1). The mean $^{87}Sr/^{86}Sr$ of all streams were statistically different at very high levels of confidence (α=0.00001; Rose and Fullagar, 2004) indicating that each stream is characterized by its own strontium isotopic signature. The highest ratios ($^{87}Sr/^{86}Sr_{average}$ = 0.7172) were observed in the terminal Middle Oconee River basin and the lowest ratios were observed in the two small Indian Creek watersheds (Table 1).

Strontium ion concentrations and strontium isotopic ratios did not vary as a function of time within a given watershed (Figure 3). The strontium isotope ratios were the most temporally invariant of all parameters in stream base flow including specific conductance (coefficient of variation = 5-10%), environmental tritium (coefficient of variation = 4-25%) and $\delta^{18}O$ (coefficient of variation = 5-7%). These results suggest that those processes responsible for geochemical and isotopic variation within base flow for a given basin (such as variable source area contributions) do not affect strontium isotope ratios. $^{87}Sr/^{86}Sr$ ratios become integrated and homogenous within a given watershed over a wide range of base flow rates that occur during the course of a year. Hence, these ratios provide the best geochemical or isotopic "signature" for base flow within a given Piedmont basin.

The intra-basin $^{87}Sr/^{86}Sr$ variation within stream base flow occurred without much change with respect to strontium ion concentrations (Figure 4). Average Sr concentrations varied only between 22-24 ppb in the four basins. Average $^{87}Sr/^{86}Sr$ were lowest within the two small Indian Creek watersheds (0.7127 - 0.7133) and were highest within the terminal Middle Oconee River basin (0.7172).

The lithology of the study area is dominated by amphibolite, mica shcist, and biotite gneiss; however, $^{87}Sr/^{86}Sr$ ratios in the underlying bedrock are not yet known. A hypothetical explanation for this trend (increasing ratios with increasing watershed area)is that flow paths in the larger Middle Oconee River basin are likely longer than within the other sub-basins. The longer flow paths, in turn, may integrate a greater contribution from Rb-bearing minerals such K-feldspar, biotite, and muscovite which will result in increased $^{87}Sr/^{86}Sr$ ratios in base flow.

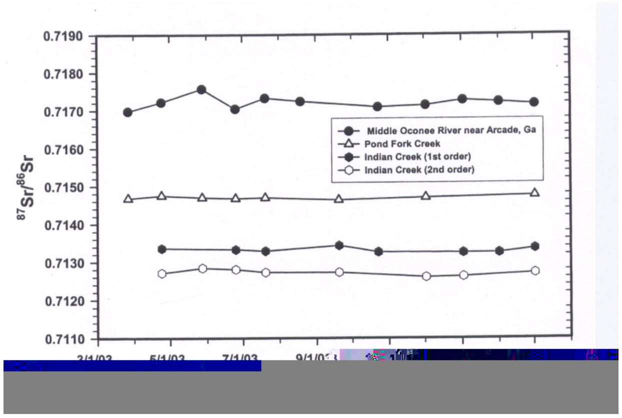

Figure 3. Temporal variation for the four stream basins within the Middle Oconee basin study area. Note: error bars are approximately the same size as the symbols.

CONCLUSIONS

Three notable features related to the evolution of strontium isotope ratios were inferred with respect to base flow in the Middle Oconee River basin. First, strontium isotope ratios were temporally invariant at a given sampling location and were not related to the rate of base-flow discharge or any other seasonal or hydrological trend. Second, each of the four sub-basins analyzed within this 860km^2 study area was characterized by its own unique $^{87}Sr/^{86}Sr$ "signature". Third, strontium isotope ratios apparently increased with basin area, independent of Sr ion concentrations. Such variation might be the result of subtle mineralogical controls (i.e. the integration of more Sr-87 from the weathering of K-feldspar, biotite, and muscovite) in the larger basins.

The time-invariant and unique ratios associated with a given basin should enable future studies to utilize Sr-isotope ratios as "natural tracers" for stream base flow. One possible application might involve the use of Sr isotopes in mass balance studies to analyze flow contributions from individual streams within a large integrated watershed.

REFERENCES CITED

Bullen, T.D. and Kendall, C., 1998. Tracing of weathering reactions and water flowpaths: a multi-isotope approach. In: (Eds.) Kendall, C. and McDonnell, J.J., Isotope Tracers in Catchment Hydrology, Ch18, Elsevier, Amsterdam,611-616.

Douglas, T.A., Chamberlain, C.P., and Blum, J.D., 2002. Land use and geologic controls on the major elemental and isotopic ($\delta^{15}N$ and $^{87}Sr/^{86}Sr$) geochemistry of the Connecticut River watershed, USA. *Chemical Geology* 189, 19-34.

Figure 4. A possible evolutionary path for Sr isotopes in Piedmont watersheds. Note that a principal feature of this suggested path is that Sr isotope ratios increase with basin area and this is not accompanied by related increases with respect to Sr ion concentrations.

Miller, M.L, Blum, J.D., and Friedland, A.J., 1993. Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes. *Nature* 362, 438-444.

Palmer, M.R. and Edmond, J.M. 1992. Controls over the strontium isotopic composition of river water. *Geochemica et Cosmochimica* 56, 2099-2111.

Rose, S. 2004. A combined hydrological, geochemical and isotopic approach to understanding the effects of basin scale on base flow systematics in the Georgia Piedmont Province. Technical Completion Report for the Georgia Water Resources Institute FY 2003, 90p.

Rose, S. and Fullagar, P.D. (2004, in review). Strontium isotope systematics of base flow in Piedmont Province watersheds, Georgia (USA). submitted to *Applied Geochemistry*.

U.S. Geological Survey, 2004. USGS 022174745 Middle Oconee River near Arcade, GA. http:waterdata.usgs.gov/

ACKNOWLEDGMENTS

We gratefully acknowledge funding for this study from the Georgia Water Research Institute (FY 2003) and Georgia State University. We would like to express our great appreciation to Jerry Waddell and Eugene Carlson of the Jackson County Water and Sewage Authority for facilitating our ground water monitoring in the study area.

Table 1. Summary of Key Isotopic and Geochemical Results (after Rose, 2004)

	Middle Oconee Basin	Pond Fork Creek	Indian Creek (2nd order)	Indian Creek (1st order)	Ground Water	Rainfall
Basin Area (km2)	860	54	3.9	12.7	-----	-----
No. of Isotopic Analyses	11	8	8	9	6	5
Average [Sr] ppb	23.6	21.8	24.2	24.2	6.1	5
Range $^{87}Sr/^{86}Sr$	0.7170-0.7176	0.7146-0.7148	0.7126-0.7128	0.7133-0.7134	0.7113-0.7125	0.7109-0.7122
Average $^{87}Sr/^{86}Sr$	0.7172	0.7147	0.7127	0.7133	0.7120	0.7117
Average Specific Conductance [μS/cm]	81.9	74.2	78.4	92.6	21.0	-----
Average Alkalinity [mg/L]	27.7	26.5	30.6	35.9	4.0	-----
Average pH	6.70	6.82	6.74	6.56	5.17	-----