GEOCHEMISTRY AND HYDROCHEMISTRY OF THE OCONEE RIVER BASIN

Mark D. Cocker

AUTHOR: Advanced Geologist, Georgia Geologic Survey, 19 MLK Jr. Dr., S.W., Atlanta, Georgia 30334.
REFERENCE: *Proceedings of the 1995 Georgia Water Resources Conference*, held April 11 and 12, 1995, at The University of Georgia, Kathryn J. Hatcher, Editor, Carl Vinson Institute of Government, The University of Georgia, Athens, Georgia.

Abstract. This study documents the background geochemistry and hydrochemistry of the Oconee River Basin (ORB) as part of the Comprehensive Basin Management Plan (SB 637), focussing on the distribution of heavy metals. The primary databases used were those of the U.S. Department of Energy's National Uranium Resource Evaluation Program (NURE), which provide a comprehensive sample coverage of the basin and a late 1970's baseline with which to evaluate more recent data. A Geographical Information System (GIS) was used to: 1) select geochemical and hydrochemical data which exist for the ORB; 2) provide statistical description of the data; 3) contour the geochemical and hydrochemical data; and 4) select individual geologic units for interpretive purposes.

The study shows that most of the geochemistry and hydrochemistry are related to regional and local geology. Some anomalously high heavy metal analyses, particularly for lead, may be related to anthropogenic activities.

INTRODUCTION

This paper summarizes a study which documents the natural background geochemistry and hydrochemistry of the ORB (Cocker, in review). The natural hydrochemistry of streams and rivers is principally controlled by the rocks and sediments through which the water flows. Background geochemistry is an important tool with which to evaluate the hydrochemistry of the surface water and to plan the maintenance of water quality. The GIS is used to catalog and analyze baseline geochemical and hydrochemical data.

Anomalously high concentrations of heavy metals may be derived from mineral deposits, rock types that contain concentrations of heavy metals above amounts found in average crustal rocks, and weathering processes which may concentrate heavy metals from rocks which do not contain large amounts of these metals.

Description of the Oconee River Basin

The ORB extends southeast from Hall County across the Piedmont and halfway across the Coastal Plain physiographic provinces. The basin includes parts or all of 27 counties, as well as the cities of Athens, Milledgeville and Dublin. The ORB is about 60 km wide, 270 km long, and covers 13,820 km^2.

Sixty percent of the basin is underlain by crystalline metamorphic and igneous rocks of the Piedmont. The remaining portion is underlain by Coastal Plain sedimentary units. Differences in chemical composition, porosity and permeability, and origin of the different rock units appear to influence the composition of the stream sediments derived from those lithologies and the water which drains through the rock units and stream sediments. The Piedmont is divided roughly into two major tectonostratigraphic terranes by the Towaliga Fault Zone. To the north are mainly metasedimentary and metagranitic rocks of the Inner Piedmont terrane. Metavolcanic rocks and granitic intrusions of the Carolina terrane are south of the Towaliga Fault Zone. The Coastal Plain consists of sandy and clayey sediments near the Fall Line and sandy sediments in the southernmost end of the ORB. Calcareous sediments are located roughly within the middle third of the Coastal Plain.

Agricultural practices during the 1800's and early 1900's caused severe erosion throughout the region. Vast quantities of sediment choked streams and raised local base levels. Stream discharge through these sediments has increased the availability of metals in the sediments to mobilization into the water. As conservation practices stabilized erosion, the streams began to entrench into the thick accumulations of sediments (Trimble, 1969). More than 90 percent of the transport of most heavy metals in river systems is shown to be as a solid phase in sediments (Horowitz, 1991). Mobilization of these sediments into the major rivers and eventually into reservoirs may concentrate metals in primary water supplies.

Databases

The use of preexisting data was an important consideration in this investigation because of time and cost. The most comprehensive, largest, and highest quality of the geochemical and hydrochemical databases for Georgia are those generated by the NURE Program to assess the uranium potential of the United States. The focus of this study is on the analyses of stream sediments and stream water. These data are available for four 1° x 2° National Topographic Map Series (NTMS) quadrangles which cover the ORB (Hoffman and Buttleman, 1994). In addition, rock, soil and saprolite samples were collected for the Athens quadrangle. Each of the 792 NURE stream sediment sample sites within the ORB represents 17 km^2 of the basin. Because the NURE samples were collected within a short period (1976 to 1978), analysis was by the same laboratory, and by the same analytical procedures, the NURE databases provide a critical baseline for subsequent investigations. Details regarding sample collection and analysis are given by Ferguson (1978). The metals in the stream sediments examined in this study include: aluminum (Al), beryllium (Be), chromium (Cr), cobalt (Co), copper (Cu), nickel (Ni), zinc (Zn), iron (Fe), manganese (Mn), titanium (Ti) and vanadium (V). Other significant primary pollutants were not analyzed during the NURE program. Conductivity, pH and alkalinity of water at the stream sediment sample sites were also included in this investigation.

Regional Background Geochemical Research

The principal previous investigation in Georgia, the Geochemical Atlas of Georgia (Koch, 1988), involved computer generation of point maps of NURE data at a scale of 1:1,785,000 for the entire state. Symbols at each sample site represent a percentile class of 25 in the analytical data. Although regional trends are evident, the maps are not useful for more detailed studies. Since the production of the geochemical atlas, significant advances in computer technology and GIS software allow rapid manipulation of the geochemical data, the incorporation of other databases, and further interpretation of the various data sets relative to each other. During the past decade, several states and countries have begun applying this technology to manage the vast amounts of surficial geochemical data for environmental and mineral resource studies (Reid, 1993; Painter et al., 1994).

METHODS

Arc-Info, a computer-based GIS, is used to link and analyze the geochemical databases with geologic and geographic information and to develop new information from these databases. The various databases are spatially related and can be plotted geographically relative to each other and at the same scale. The geographical, geochemical, and geological databases that are used in this project are derived from a variety of different sources, have different geographical extent, are originally at different scales and projections, and contain different types of data. These data include: 1) stream sediment sample points, wells, rock samples, water samples, and mines; 2) stream and road segments; and 3) geologic, hydrologic, and political units.

The Georgia Geologic Survey, a branch of Georgia's Environmental Protection Division, and the Water Resources Division of the U.S. Geological Survey cooperatively develop and maintain a GIS for the State of Georgia. The GIS databases used in this project include: 1) hydrography, 2) hydrounits, 3) county boundaries, 4) geology, 5) major lakes, 6) major roads, 7) soils, and 8) land use data. GIS databases created during this project include: 1) NURE geochemical and hydrochemical data, 2) Georgia Environmental Protection Division hydrogeochemical data, 3) mines and prospects, and various geochemical databases derived from files and publications of the Georgia Geologic Survey and the U.S. Geological Survey, and student theses. Contoured geochemical maps were produced with Arc-Info at a scale of 1:500,000. The GIS selected specific rock units and sample sites that are found within those rock units.

RESULTS

Hydrochemistry of the Oconee River Basin

The ORB crosses two regions or zones of streams with pH higher than 7.0, conductivities greater than 50 microohms/cm, and alkalinities greater than 0.3 meq/L that separate three regions of lower pH, lower conductivities and lower alkalinities. These zones are spatially related to regional geologic and related geochemical trends. In the northern half of the ORB, the zones of higher alkalinity, conductivity and pH coincide with the extent of the metavolcanic and metavolcaniclastic rocks of the Carolina terrane and are distinguished from the generally metasedimentary and metagranitic rocks of the Inner Piedmont terrane, which have lower pH, conductivity and alkalinity. Within the Carolina terrane, smaller zones of higher alkalinity, conductivity and pH generally correlate with the spatial distribution of ultramafic and mafic rocks such as serpentinites, norites, gabbros, diorites, amphibolites, and amphibolitic gneisses. In the Coastal Plain the zones of higher alkalinity, conductivity and pH correlate with the limestones and marls of the Suwanee Limestone, the Ocala Limestone and the Twiggs Formation. Zones of low pH, conductivity and alkalinity are underlain by sandy sediments and clays of Cretaceous, Eocene and Miocene formations.

Stream Sediment Geochemistry of the Oconee River Basin

Most stream sediments in the Coastal Plain contain less than 20,000 parts per million (ppm) Al, whereas stream sediments in the Piedmont generally contain greater than 30,000 ppm Al. Tertiary-Cretaceous sediments may contain up to 169,000 ppm Al, possibly associated with kaolin deposits. Within the Piedmont, the highest mean concentration of Al (70,000 ppm) occurs in the Carolina terrane. High Cr values (> 5 ppm) lie along NE-trends which correlate with ultramafic rocks and fault zones which may contain sheared ultramafic rocks. A large Cr anomaly in Hall County may be related to ultramafic rocks within the Brevard Fault Zone. Co is highest in the Carolina terrane with concentrations commonly greater than 10 ppm. Rock units with high Co include: ultramafic rocks, hornblende gneisses, and gabbro. Stream sediment Cu anomalies (> 10 ppm) are larger and more abundant in the Carolina terrane than in the Inner Piedmont. Alignment of Cu anomalies are similar to linear trends defined by the base metal mines in the Carolina terrane, brittle faults and diabase dikes. A Cu anomaly which follows the northeast trace of the Brevard Fault Zone in Hall County may be related to the same source rocks for the Cr anomaly. High Pb concentrations occur as single point anomalies which are near population centers and may be anthropogenic. Some anomalous Ni values are coincident with anomalous Cr and suggest an association with ultramafic source rocks. Higher Ni values within the Carolina terrane, particularly west of the Oconee River, suggest an association with metabasaltic rocks (amphibolites). A region of anomalously high Zn (30 to 253 ppm) lies within the western part of the Carolina terrane. A common association of Zn and Ni with metabasalts suggests that those sediments are derived from metabasalts. Linear trends in some Zn anomalies may indicate structural controls similar to those noted for Cu.

Iron has an important influence on water quality and provides important information regarding the effects of lithology on water quality, particularly within the ORB. The tendency of Fe to form oxide or hydroxide crusts may cause the precipitation or absorption of heavy metals. Organic-free waters lose their oxidizing character by reaction with ferrous Fe silicates, such as biotite, chlorite, amphiboles, pyroxenes, or by contact with sulfides or ferrous Fe carbonates. The Fe compounds may be quantitatively the most important inorganic reducing agents. Because of silicate hydrolysis and carbonate dissolution, pH tends to rise, and the environment becomes alkaline as well as reducing. Sediments containing the highest Fe concentrations (up to 443,000 ppm) are located within the Carolina terrane and reflect the presence of amphibolitic rocks. Correlation of high amounts of Fe in stream sediments with higher stream pH suggests that hydrolysis of Fe-bearing silicates may be an important control on pH.

Correlation coefficients for analyses grouped by rock unit suggest the following associations: Zn-Co-Cu-Ni; Fe-Mn-Ti-V-Mg-Al-Na; and Be-K. The Zn-Cu-Co-Ni association may indicate the presence of Zn-Cu-Co-Ni bearing sulfides. The Fe-Mn-Ti-V-Mg-Al-Na association is related to sodic plagioclase, Fe-Mg silicates and Fe-Ti-V-Mn oxides in the metavolcanic rocks in the Carolina terrane. A granitic or pegmatitic association is suggested by the relation of Be and K. The lack of any correlation of Pb with other metals may indicate a different source for the Pb.

Although stream sediments were not analyzed for As, 38 samples of rock, soil and saprolite in the Athens quadrangle were analyzed for As. Of these samples, 80 percent contained greater than 100 ppm As, and 30 percent contained 250 to 825 ppm As. The As may be related to a base-metal trend which extends into the ORB from the southeast, or the As may be a residue from pesticides used on cotton crops earlier in this century.

Potential Contamination

Some isolated sample sites with high concentrations of heavy metals, and pH, conductivity and alkalinity measurements that differ from background values are associated with human activities noted in the NURE databases. These activities are listed as urban, dump (sanitary landfill) and sewage, but details concerning the nature of these activities are not in the NURE databases. Many of these sites are near Milledgeville and immediately south of the Fall Line. One particular sample contained 525 ppm Pb, 125 ppm Zn, and 31 ppm Cu. The stream water pH was 9.2, and conductivity was 180 micromhos/cm. Because correlation of Pb with other metals by rock unit is lacking, the sources for high Pb in sediments in the ORB may be anthropogenic. Further field and laboratory work is needed to verify the analyses and the sources.

SUMMARY AND RECOMMENDATIONS

The NURE databases provide important baseline geochemical and hydrochemical data for the ORB. These data indicate that regional geology and local geology are the most important factors controlling the geochemistry and hydrochemistry. Localized anthropogenic activities may affect some of the stream sediments and stream water.

Past agricultural practices resulting in severe erosion and deposition in the stream channels have affected and may continue to influence stream sediment geochemistry and hydrochemistry.

Major compositional differences between the Inner Piedmont terrane and the Carolina terrane are important factors controlling the distribution of metals in stream sediments and the hydrochemistry of stream water. Within the scope of this study (Cocker, in review), Al, Cr, Co, Cu, Ni, Zn, Fe, Mn, Ti and V are the most significant metals. Stream sediments derived from the metavolcanic rocks of the Carolina terrane contain higher concentrations of these metals. Streams within the Carolina terrane have a distinctly higher pH, conductivity and alkalinity than streams within the Inner Piedmont terrane. Increased hydrolysis of silicates and dissolution of carbonates in the metavolcanics may account for these differences.

The presence of base metal sulfides is suggested by the Zn-Cu-Co-Ni association in the ORB stream sediments. Base and precious metal sulfide mines in the metavolcanic rocks of the Carolina terrane east of the ORB contain significant concentrations of Au, Cu, Pb, Zn, Fe, Mn, Ba, As, Bi, Cd, Cr, Hg, Tl, Mo, Sb, Te, V, and Ag (Tockman et al., 1993; Maddry et al., 1993). Similar mineralization may exist in the same or similar rock units within the ORB. The NURE stream sediment geochemistry and stream hydrochemistry suggests similar compositions over much of the Carolina terrane. Metals such as Hg, As and Sb that were not analyzed in the NURE stream sediment geochemistry program may be present within the ORB in locally high concentrations.

Differences in composition and porosity of Coastal Plain sedimentary units also affect stream sediment geochemistry and stream hydrochemistry. Streams within the Coastal Plain draining sandy and clayey sediments have distinctly lower pH, conductivities and alkalinities than those streams which are spatially associated with calcareous sediments. The calcareous sediments buffer the stream pH, and their weathering contributes to higher conductivities. High porosities and relatively non-reactive quartz sands leaves rain water essentially unchanged with low pH, conductivities and alkalinities.

ACKNOWLEDGMENTS

The author gratefully acknowledges the help of A. Sandercock, D. Hipple, and V. Trent in the production of the GIS maps used in this study and the reviews of R. McDowell and B.J. O'Connor.

LITERATURE CITED

Cocker, M.D., in review. Distribution of selected elements in stream sediments, stream hydrochemistry and geology of the Oconee River Basin, Georgia: Georgia Geologic Survey Bulletin.

Ferguson, R.B., 1978. Preliminary raw data release, Greenville 1° X 2° NTMS area, Georgia, North Carolina, and South Carolina, SRL Document DPST-78-146-2: E.I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, South Carolina, 149 pp.

Horowitz, A.J., 1991. *A Primer on Sediment-Trace Element Chemistry*: Lewis Publishers, Chelsea, Michigan, 136 pp.

Hoffman, J.D., and Buttleman, K.P., 1994. National Geochemical Data Base: National Uranium Resource Evaluation Data for the Conterminous United States: U.S. Geological Survey Digital Data Series DDS-18-A, 1 CD-ROM.

Koch, G.S., Jr., 1988. A geochemical atlas of Georgia: Georgia Geologic Survey Geologic Atlas 3, 13 pl.

Maddry, J.H., Speer, and Rucker, P.D., 1993. Whole rock and trace element geochemistry of rocks from the Snake deposit, Haile gold mine, Lancaster County, South Carolina: *South Carolina Geology*, v. 35, p. 27-36.

Painter, S., Cameron, E.M., Allan, R., Rouse, J., 1994. Reconnaissance geochemistry and its environmental relevance: *Journal of Geochemical Exploration*, v. 51, p. 213-246.

Reid, J.C., 1993. A geochemical atlas of North Carolina, USA: *Journal of Geochemical Exploration*, v. 47, p. 11-27.

Tockman, K., Cherrywell, C.H., 1993. Pathfinder geochemistry for the South Carolina gold deposits: *South Carolina Geology*: v. 35, p. 79-83.

Trimble, S.W., 1969. Culturally accelerated sedimentation on the middle Georgia Piedmont: Unpublished M.S. Thesis, University of Georgia, 110 pp.