

SURFACE GEOCHEMISTRY OF MISSISSIPPI TO BE SURVEYED

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INTRODUCTION

The Mississippi Office of Geology is participating in a regional soil and sediment geochemical sampling program with the state geological surveys of Alabama, Georgia, and Florida and the U.S. Geological Survey (USGS). Over a year of planning and training went into the implementation of this project.

The objectives of the project are to 1) determine baseline (naturally occurring) values for chemical elements based on stream sediment and soil samples, 2) prepare statistically reliable geochemical maps for individual elements where possible, and 3) identify areas favorable for mineral exploration. The soil and sediment sampling program, the first state-wide effort in Mississippi, will yield important information regarding the state's mineral and environmental characteristics.

BACKGROUND

The existence, quality and survival of life depend upon the availability of elements in the correct proportions and combinations. Sometimes where certain chemical elements are present in excessive or deficient quantities, there may be some risk to humans, animals, or plants. Therefore, it may be both useful and important to determine the present abundance and spatial distribution of the elements across the Earth's surface in a systematic manner.

The history of systematic geochemical surveys in the United States began in the late 1960s. The USGS developed its first national geochemical database in 1968. The data set was given the acronym RASS (Rock Analysis Storage System) and contained a large quantity of geochemical exploration data gathered across the country by the USGS. The geochemical data are primarily from analyses of stream

sediments and soils from potential uranium-bearing igneous and metamorphic terranes of the "hard rock" west and east, but geochemical analyses of rock, soil, sediments, and sometimes plants were conducted for exploration for other metals, such as copper, lead, zinc, and nickel.

In the early 1970s, the USGS developed a second geochemical database known as PLUTO. PLUTO continued to incorporate small-scale geochemical survey data gathered by the USGS, as well as a large quantity of geochemical analyses done mainly on rocks and ores by a multitude of USGS projects. The RASS and PLUTO data sets are currently being released by the USGS on CD-ROM (Baedecker et al., 1998).

In the mid-1970s, the National Uranium Resource Evaluation program, or NURE program, was begun. The program was funded and managed by the newly created Department of Energy. The NURE program gathered data to evaluate uranium resources for the United States and to identify areas favorable for uranium deposits (Averett, 1984). Between 1975 and 1983, the NURE program acquired ground-based geochemical data and airborne spectral gamma-ray radiation data for much of the conterminous 48 states and Alaska.

The Hydrogeochemical Stream Sediment Reconnaissance (HSSR), one component of the NURE program, en-

tailed collection and analysis of samples of sediment (stream, soil, talus, playa, and others), ground water, surface water, and vegetation to determine concentrations of uranium and other selected elements (Arendt and others, 1980). These data helped to outline geochemical provinces and to show favorable areas for more detailed investigation. Averett (1984) gives tabulations of areas surveyed during the HSSR and the available information for those areas.

Another component of the NURE program was aerial gamma-ray surveying. These NURE data compose the only nationwide data set on natural radiation in the environment. The U.S. Geological Survey has reprocessed the aerial gamma-ray data to produce maps showing surface concentrations of potassium (K), uranium (U), and thorium (Th) for the conterminous United States (Duval and others, 1989, 1990; Phillips and others, 1993).

HSSR data reports were issued for 330 (70.5 percent) of the 468 1°x2° quadrangles in the 48 conterminous states and for 104 (68 percent) of the 153 quadrangles in Alaska. Thus, about 70 percent of the nation has such geochemical coverage. Almost all samples were analyzed for uranium, and most were analyzed also for as many as 59 elements (Averett, 1984).

By the early 1980s the NURE database consisted of 894

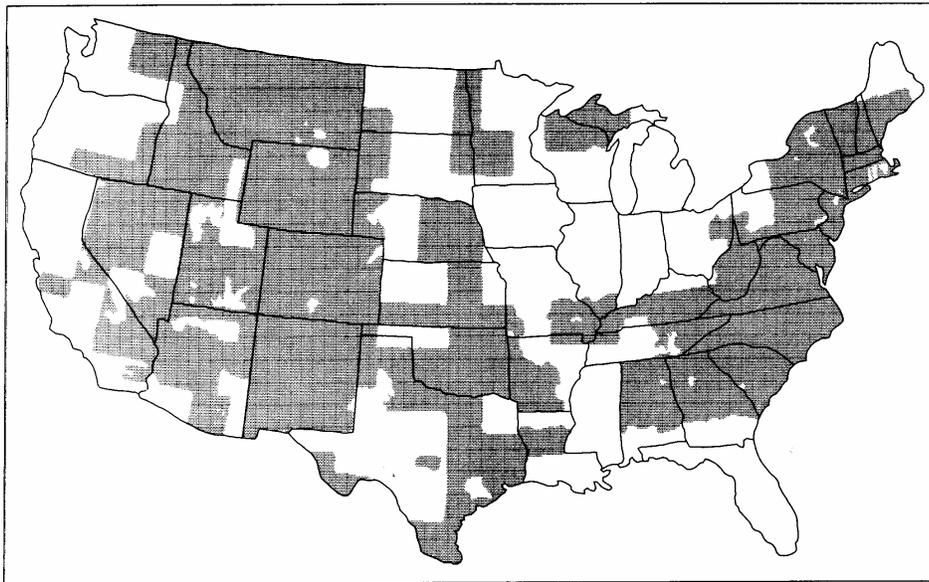


Figure 1. NURE sample location map for the conterminous U.S.

files in 49 different formats. For this reason, the University of Oklahoma was funded to compile and synthesize the various formats into one. They managed to combine 817 of the 894 files into one format before funding ran out. So the format problem, while improved, remains an obstacle when considering the entire database.

In 1985, and by agreement with the Department of Energy, since the NURE program had concluded, the USGS became the repository for the NURE data, samples, and field maps. Currently, the USGS maintains the National Geochemical Data Base composed of all three databases. The geochemical data for all quadrangles surveyed in the conterminous states are available on compact disc (Hoffman and Buttleman, 1994, 1996); the geochemical data for the western states are also available separately on compact disc (Hoffman and others, 1991); data for Alaska were released by Hoffman and Buttleman (1996).

Significantly, throughout the course of these previous geochemical sampling efforts, Mississippi was not a high priority target, and consequently very little is known about its geochemical characteristics (Figure 1).

The current sampling program in Mississippi will be incorporated into the National Geochemical Data Base. Sample materials include stream sediment, soil, bedrock, surface water, ground water, and vegetation. With respect to the NURE database, stream sediment sample coverage dominates over other types of sampling, and is generally thought to be the most useful type of sample in assessing mineral resource potential and determining geochemical backgrounds. Stream sediments generally represent a composite of materials shed from upstream areas and, when properly sampled, provide averaged geochemical signatures derived from rock units and soils within the drainage basin.

Ideally, bedrock or mineral specimens of interest could be analyzed to determine a "fingerprint" which might be compared to stream sediment analysis in order to identify terranes which are consistent with a particular mineral deposit type. Soil samples, on the other hand, are considered point-source data and are thought to be less useful in determining the overall elemental constituents of an area, but must be utilized in areas where suitable streams do not exist. However, soil samples typically provide site-specific geochemistry—the type of data most valuable to soil scientists and agricultural stakeholders.

METHODS AND TECHNIQUES

The planning effort for Mississippi identified the desired sample type and the number of samples required for regional coverage. It was decided that stream sediment samples would best characterize the state's overall geochemical make-up for this initial investigation, except for the "Delta" region, where soil samples were employed due to a lack of suitable streams and associated sediments. The sampling program, to be

consistent with existing geochemical data for the Coastal Plain province, and to be managed within fiscal constraints, determined that a 10 km x 10 km grid spacing of sample locations across Mississippi was the optimum sampling objective. This was a convenient grid size since Universal Transverse Mercator (UTM) projection lines provide just such a framework on USGS topographic maps. For Mississippi, each 10 km x 10 km cell was given a unique sample number created from the easting and northing coordinates of the southwestern corner. The target stream population designated first order streams with drainage basins in the range of 2 - 10 km². Suitable streams within the cells were randomly selected for sampling by coin toss. The coin toss procedure was as follows: 1) Quarter the cell. 2) Flip a coin to select the northern or southern half. 3) Flip again to select the eastern or western half. 4) Repeat for each cell to be sampled. Furthermore, within that quarter cell randomly selected, the ideal sediment sample should be taken from the upstream side of bridge crossings in order to avoid downstream dumping scenarios.

In the "Delta" region soil sample sites were also selected within cells randomly, via a series of coin tosses. Most sample locations were situated near roads for convenience, but far enough away to avoid fill material. A minimum of three hand auger samples of the plow zone (upper 22 cm) were taken, about 35 meters apart, in a triangular spacing, and composited. This procedure reduces sampling errors and fosters the development of statistically reliable geochemical maps.

The geochemical sampling project includes an analysis of variance (AOV) in order to provide even coverage and to test differences in stream sediment chemistry 1) between cells, 2) within cells, 3) within streams, and 4) between chemical analyses. Approximately 5 percent of the cells were selected for AOV sampling and were chosen with the assistance of a random numbers table. For these AOV cells, a second stream location is randomly selected for sampling, along with an upstream sample to be split for analysis. Sampling for AOV purposes was carried out for soil sampled regions also.

An essential component in collecting a sample that represents the stream's geochemistry is compositing. Ideally, 6 to 10 depositional zones within a 100-meter-long stream reach containing fine-grained particulate matter at each site are sampled, with the goal being to select depositional zones that represent upstream influences and various flow regimes. This practice reduces the local-scale variability and allows for a more accurate representation of the average geochemical values at the site. Keeping sampling error at a minimum improves the possibility of being able to produce a stable geochemical map. The data will be used to determine geochemical baselines of statistically known reliability. Study of the data is likely to identify geochemically unusual samples or samples that represent specific types of mineral deposits.

A number of these will be analyzed in more detail geochemically and mineralogically to help determine the mode of occurrence of the elements in the samples. Such information is often useful for mineral exploration and environmental purposes.

Sampling was begun in September of 1997 and continued at a frantic pace through the first week of April of 1998. Field work and sample collection were performed primarily by two individuals of the Office of Geology's Surface Geology Division—David Thompson and Seth Berman. Several individuals of the Environmental Geology Division also provided much-appreciated help in collecting samples: Trey Magee, Archie McKenzie, and Robert Ingram. During this 7-month period, 1,462 samples were collected statewide (Figure 2).

A field sheet was completed for each sample location in order to characterize the setting in a manner useful for the project and for future reference. Recorded information includes: geology, latitude/longitude ascertained by global positioning system (GPS), elevation, relief, vegetation, channel width, water depth, water color, stage, flow rate, setting,

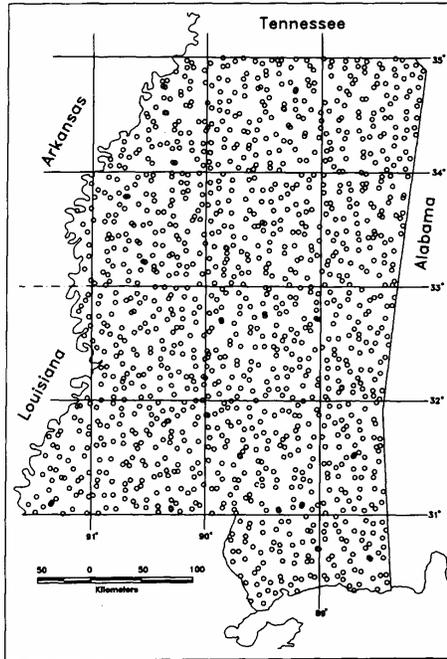


Figure 2. Location map of the 1,462 sample collection sites from Mississippi utilized in the current study.

possible contaminants, and the alkalinity of the stream water, measured with titration test kits and expressed in ppm total alkalinity as calcium carbonate.

After air drying, samples were shipped to the USGS in Denver for processing and chemical analysis. Preparation of sediment samples for chemical analyses involved screening of the bulk sediment samples through a 100 mesh (150 micrometer aperture) U.S. Standard stainless steel sieve. The -100 mesh fraction was split into analytical and archival samples. In cases where insufficient -100 mesh fraction was recovered, the sample was recombined and ground by use of a ceramic-lined grinder to pass through the 100 mesh sieve.

Analytical techniques utilized on the samples include the following.

1. ICP 40. Forty major, minor, and trace elements are determined by ICP-AES (Induction Coupled Plasma-Atomic Emission Spectroscopy) after the sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature. Elements determined and their lower and upper detection limits are given below.

Al	.005-50%
Ca	.005-50%
Fe	.02-25%
K	.01-50%
Mg	.005-5%
Na	.005-50%
P	.005-50%
Ti	.005-25%
Ag	2-10,000 ppm
As	10-50,000 ppm
Au	8-50,000 ppm
Ba	1-35,000 ppm
Be	1-5,000 ppm
Bi	10-50,000 ppm
Cd	2-25,000 ppm
Ce	5-50,000 ppm
Co	2-25,000 ppm
Cr	2-50,000 ppm
Cu	2-15,000 ppm
Eu	2-5,000 ppm
Ga	4-50,000 ppm
Ho	4-5,000 ppm
La	2-50,000 ppm
Li	2-50,000 ppm
Mn	4-50,000 ppm
Mo	2-50,000 ppm
Nb	4-50,000 ppm
Nd	9-50,000 ppm
Ni	3-50,000 ppm
Pb	4-50,000 ppm
Sc	2-50,000 ppm
Sn	5-50,000 ppm

Sr 2-15,000 ppm
Ta 40-50,000 ppm
Th 6-50,000 ppm
U 100-100,000 ppm
V 2-30,000 ppm
Y 2-25,000 ppm
Yb 1-5,000 ppm
Zn 2-15,000 ppm

2. ICP 10. Ten elements are determined using ICP-AES following a hydrochloric acid - hydrogen peroxide digestion and aliquot 336-diisobutylketone extraction. Elements determined and their lower and upper detection limits are given below.

Ag 0.08-400 ppm
As 1.0-6,000 ppm
Au 0.10-1,500 ppm
Bi 1.0-6,000 ppm
Cd 0.05-500 ppm
Cu 0.05-500 ppm
Mo 0.10-900 ppm
Pb 1.0-6,000 ppm
Sb 1.0-6,000 ppm
Zn 0.05-500 ppm

3. Mercury. Continuous-flow cold vapor atomic absorption spectrometry is used for the determination of mercury. Lower reporting limit is 0.02 ppm.

4. Arsenic, Antimony, and Selenium. Samples are digested using a multi-acid procedure; oxidation states of the three elements are reduced; sodium borohydride is added to the solution to form gaseous hydrides; these hydrides are stripped from the analytical stream and transported with inert gas to the atomic absorption spectrophotometer where the elements of interest are determined. Optimum analytical ranges are: As 0.6-20 ppm, Sb 0.6-20 ppm, and Se 0.2-4 ppm.

5. WDXRF—Wavelength Dispersive X-Ray Fluorescence. Major elements are determined using the method of Taggart and others (1987). This involves a lithium tetraborate fusion of the powdered sample, followed by measurement of K X-ray intensities on a Phillips PW1606 spectrometer. A wide range of USGS and NIST rock standards is used for calibration. The method has been proven to be highly accurate for most rock and sediment samples. Analytical precision is mainly determined by counting statistics, and is better than 0.05% (absolute) for most oxides (SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅ and MnO).

6. INAA—Instrumental Neutron Activation Analysis. The procedure used at the USGS is a multi-element technique capable of simultaneously determining up to about 50 ele-

ments. The technique has very high sensitivities for most of the elements that can be determined—most detection limits range from 0.05 to 50 ppm. Further, the INAA technique is highly precise and accurate—overall errors of less than 2% relative standard deviation can be achieved for many elements.

Sample aliquots weighing typically about 0.5 g are irradiated for six hours in the TRIGA reactor at the USGS, Denver, Colorado, at a flux of 2.5×10^{12} n/cm²/s. Standards consisting of spiked silicate powders are irradiated together with the samples. Following a decay period of 6-8 days, the samples and standards are counted for one hour on a pair of high purity germanium (HPGe) detectors, one coaxial and one planar, coupled to a multichannel analyzer system. After an additional 26-32 day decay period, the samples and standards are counted for two hours on a coaxial HPGe detector. The coaxial HPGe detectors have resolutions of about 1.9 KeV measured at 1.33 MeV, and efficiencies between 18 and 25%. The planar HPGe detector has a resolution of 0.80 KeV measured at 122 KeV. Gamma-ray peaks are integrated using the SAMPO program. Corrections for dead time, decay during counting, and spectral interferences are made using an in-house data reduction program to calculate elemental concentrations. Samples of SAR-L, SAR-M (USGS analytical standards) and/or NIST2710 are included in each irradiation as quality control standards.

ANTICIPATED BENEFITS

So what kind of benefits can the State of Mississippi expect to realize from this ambitious project? The Mississippi Office of Geology is contacted frequently by environmental engineering firms and other interested parties requesting data on naturally occurring levels of potentially dangerous chemical elements at specific sites in Mississippi. As Figure 1 illustrates, that type of information has not been available, and only average elemental levels for the southeastern Gulf Coastal Plain at large could be cited. As a result of this effort, geochemical data will be available for small watersheds all across Mississippi. Currently, analysis of the samples is underway and should be 90% completed by the fall of 1998.

This type of geochemical data has wide-ranging environmental use. For example, one will be able to consider the natural concentration of lead in sediments of southwestern Noxubee County prior to industrial development, or compare a known mercury-contaminated site in Hinds County to surrounding baseline, naturally occurring levels.

These data will have considerable mineral assessment/exploration potential (for example, Grosz and Schruben, 1994) and will supplement the existing NURE aeroradiometric coverage. It is anticipated that heavy-mineral-bearing (ilmenite, rutile, zircon, and monazite) prospective terranes will be recognized in the Cretaceous and Tertiary outcrop

belts in Mississippi, an extension of known prospects in Alabama and Tennessee. A poorly understood thorium-dominated aeroradiometric anomaly associated with the Jackson Group will be investigated. It may represent a previously unrecognized deposit type for placer resources. Additionally, prospective terranes for kaolin, bauxite, and uranium may be recognized as a result of this sampling program. As unusual geochemical situations are identified, it is expected that additional follow-up sampling by the Mississippi Office of Geology will be conducted.

The geochemical data can be utilized to create interpretive derivative maps involving polygons of watershed, lithology, geology, mineral deposits, and political boundaries.

The first likely publication related to the data will be a series of Open-File Reports with listings of concentrations of chemical elements in spreadsheet form. Later, the Mississippi Office of Geology in collaboration with the USGS anticipates the publication of a geochemical atlas or maps that will highlight the distribution of particular chemical elements, combinations of chemical elements, and elemental

ratios. It is anticipated that these data also will be available on the Internet at USGS and Mississippi Office of Geology Web sites.

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Figure 3. David Thompson collects stream sediment sample #27360 along a tributary of Tuscolameta Creek in northeastern Scott County. Photograph by Cletus Magee, November 6, 1997.

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