Solid-phase geochemical survey of the State of Mississippi; an atlas highlighting the distribution of As, Cu, Hg, Pb, Se, and Zn in stream sediments and soils

David E. Thompson, RPG Office of Geology, MDEQ



Heavy or toxic metals occur naturally in the environment, but seldom in toxic concentrations. Contamination levels can result from mining, manufacturing, and the use of man-made products such as batteries, paints, fertilizers, pesticides, sewage sludge, and industrial waste. Excess heavy metal accumulation in sediment, soil and water can be toxic to humans, animals, and plants. Harmful exposure to heavy metals by man is typically chronic and associated with transport up the food chain. Ingestion of, or dermal contact with, heavy metals can cause acute poisoning, although less common.

The problem of agricultural pollution can be scrutinized from different perspectives. One perspective is that pollution is caused by agriculture; whereby heavy pesticide and fertilizer use contaminate soil, surface water, and groundwater with a variety of toxins. Another perspective involves pollution encroaching upon agriculture. Farm fields, especially those situated close to industrial sectors, are commonly impacted by off-site pollution and stand potential contamination of both soils and crops with heavy metals. Industrial wastewater, even post-treatment, may contain high levels of toxic metals and feed into streams and farm irrigation canals. Atmospheric fallout is another mode of toxic metal deposition. Taken up by crops, heavy metals may enter and contaminate the food chain. Even low levels of elements, such as arsenic, mercury, and cadmium, can be a health concern.

Disposal of sewage sludge by application to cropland has become a common practice in the United States. This practice provides valuable nutrients and organic matter to the soil. However, sewage sludge contains variable quantities of trace elements, including those termed "heavy" metals (metallic chemical elements with a relatively high density and are toxic or poisonous at low concentrations). Numerous elements can be

found in sludge, but considerable interest has been given to: cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), and lead (Pb). Copper, nickel, and zinc are phytotoxic (diminished plant growth) at high concentrations. Cadmium and lead are considered food-chain contaminants, whereby cadmium can readily enter the food-chain via plant uptake. Copper is also toxic to certain livestock. Cadmium in soils is more easily relinquished to plants than most metals and uptake is not restricted by plant phytotoxicity. Lead, conversely, is very insoluble in soil and is not easily taken up by plants.

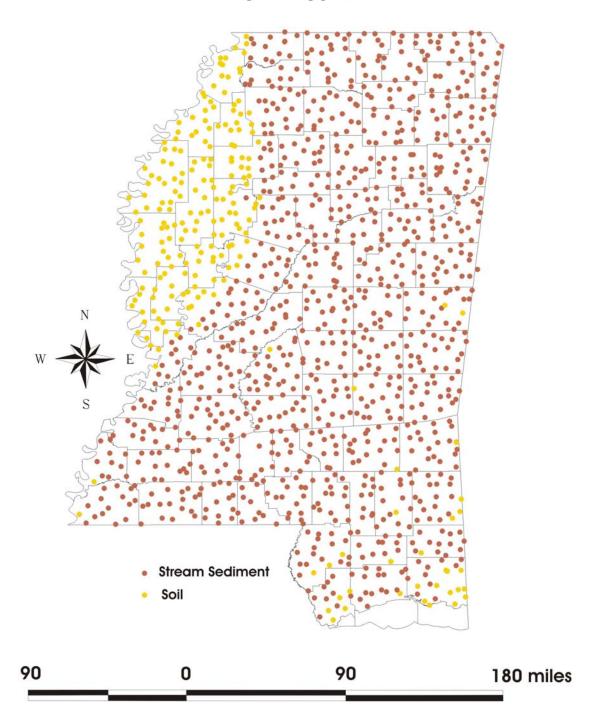
Ionic forms of toxic metals may combine with other substances to form toxic compounds. The most common problem causing cationic (positively charged) metals are mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese. Problematic anionic (negatively charged) metals are arsenic, molybdenum, selenium, and boron; and frequently combine with oxygen.

This geochemical atlas represents a "snap shot" of the surface geochemistry in the state; taken between September 1997 and April 1998 (Mississippi I Data Set). Because of the large number of samples, in addition to stable, consistent laboratory analysis, it should provide an accurate baseline representation of the overall geochemical conditions and allow for discrimination of a valid background representation. These values compare favorably to studies and values from adjacent regions. Laboratory analyses proved some anomalously high values of some elements from place to place. For instance, a stream sediment sample taken in Marshall County was shown to have unusually high levels of copper and lead, 517 and 56 ppm respectively. Any unusual results, such as this, were noted and a supplementary data collection phase was undertaken (Mississippi II Data Set). Regarding the Marshall County sample, in this instance the anomalously high copper and lead values were found to be significantly lower, corresponding well with regional levels, when the supplementary data values were obtained. A large, anomalous concentration of a substance usually corresponds to a polluted site but may not inevitably be a cause for concern. Additional characteristics of the substance, as well as the concentration, should be taken into account. Some other characteristics to consider include the quantity of the substance initially released, its rate of release, its availability to organisms, and its term of residence in a particular environmental setting.

The geochemical survey conducted in Mississippi concentrated on two sample types; stream sediment and soil (Plate 1). Stream sediment was selected as the preferred sample media in order to obtain results which best represent the geochemical make-up of a particular watershed. Soil samples, which provide point specific data, were utilized in areas where suitable streams were not available for sampling. Soil samples were primarily collected in the "Delta" (Mississippi River Alluvial Plain) and along the Gulf Coast. It is important to note that the geochemical values of sampled soils appear to be relatively higher than the stream sediment batch when considering the maps and data. For example, at a soil sample location in "The Delta" of Quitman County (Mississippi I Data Set), the arsenic concentration was 16.8 ppm. For comparative purposes, a nearby generally unsuitable, channelized stream was sampled as part of the supplemental effort (Mississippi II Data Set). The sampled stream sediment contained an arsenic concentration of 9.8 ppm.

Plate 1

Sample Types



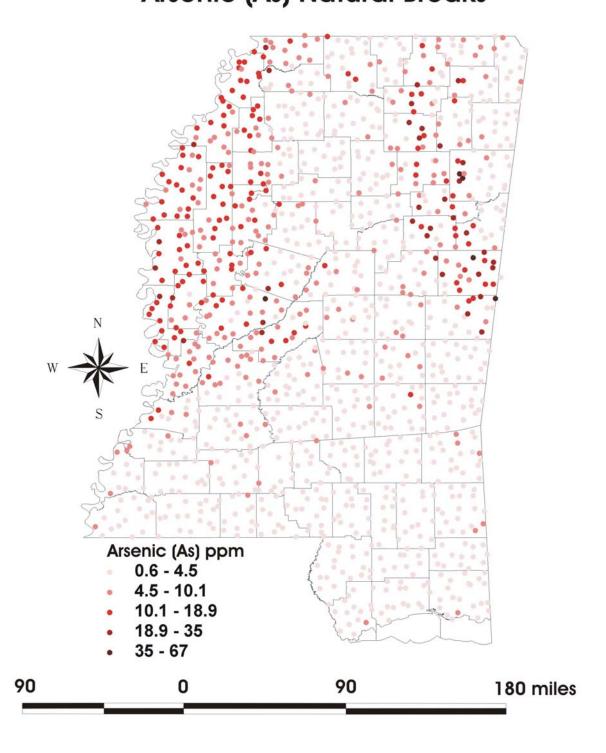
Arsenic (As)

Small amounts of arsenic, a silver-gray colored metalloid, are widespread and occur naturally in the environment. It is typically found in, and weathers from, sulfide minerals. Arsenic is also released into the air by volcanoes. However, human activity accounts for most arsenic contamination in sediment, soil, and water. In the environment, when arsenic is combined with oxygen, chlorine, or sulfur, inorganic arsenic compounds are formed. Inorganic arsenic compounds are utilized in the manufacture of wood preservatives. Organic arsenic compounds are used as pesticides and herbicides, primarily on cotton plants. Historically, arsenic use as an insecticide and herbicide has resulted in the widespread contamination of agricultural soils and water. Because arsenic is a common constituent in coal, localized air-borne contamination can occur around coal-burning facilities. Burning treated wood is not advisable, since the smoke may contain dangerous levels of arsenic compounds, as well as chromium ions and copper compounds.

Arsenic is not destroyed in the environment, conversely it may change form. Pure arsenic is not water soluble, but can be dissolved by strong acids. Many arsenic compounds will dissolve in water and can contaminate surface or groundwater. Airborne arsenic gradually settles to the ground or is washed from the air by rain. Arsenic has high acute (short-term) toxicity to animals, birds, and aquatic life. Diminished plant growth and crop yields may result in areas where soils have high arsenic content. Arsenic has high chronic (long-term) toxicity to aquatic life, and moderate chronic toxicity to animals and birds. Because arsenic is very persistent in the environment, fish and shellfish tend to bio-accumulate organic arsenic compounds; however, this compound is less toxic than inorganic arsenic compounds.

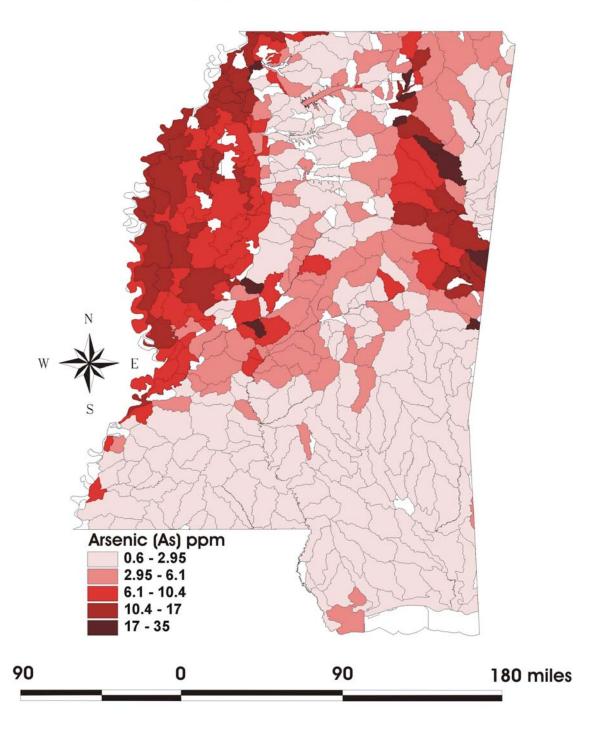
Notably, the areas with the highest arsenic concentrations in Mississippi appear to be associated with the agricultural areas of the Black Prairie, the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 2) is a point map of sample locations along with corresponding colors that relate to elemental concentration.

Plate 2
Arsenic (As) Natural Breaks



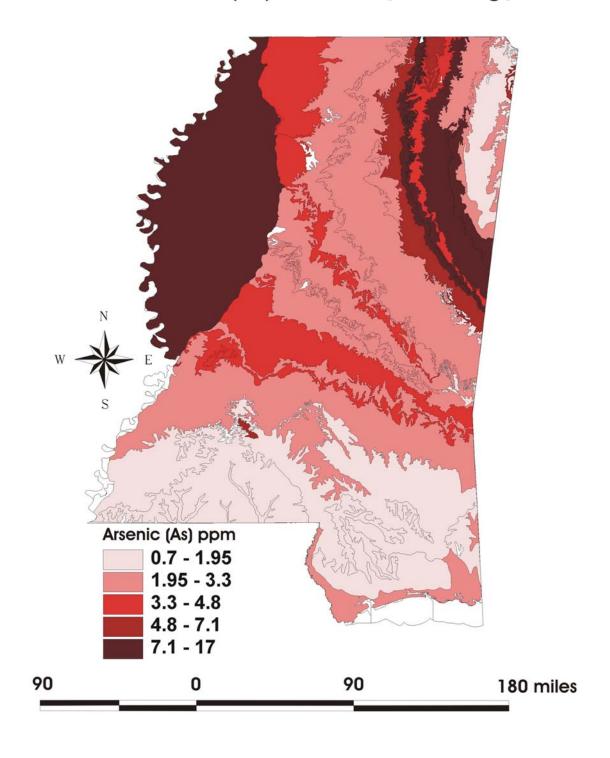
The following derivative map (Plate 3) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for arsenic.

Arsenic (As) Values By Watershed



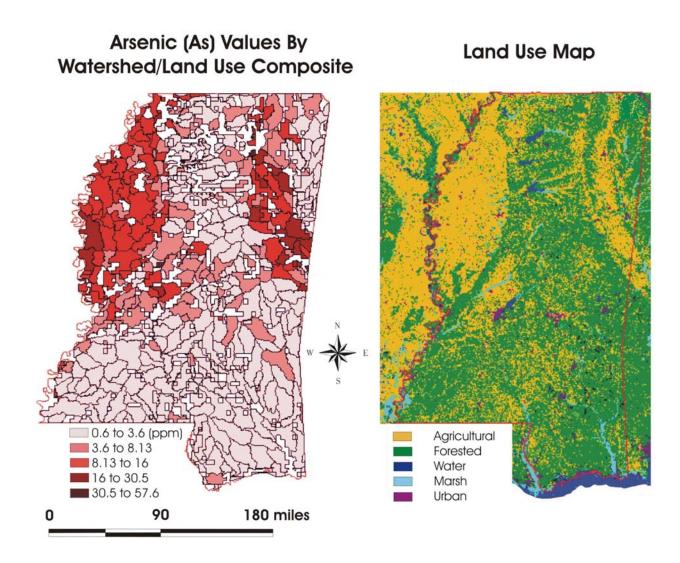
The following derivative map (Plate 4) is based on median geochemical values within a particular geologic unit. The Mississippi River Alluvial Plain, the Jackson Group, and upper Cretaceous units all reflect higher values for arsenic. These geologic units also coincide with the same high use agricultural areas mentioned previously. Interestingly, the middle Claiborne is shown to have a relatively high arsenic value. Some high arsenic values are evident on the point map near the Tennessee state line in Desoto County. It is likely that this region of extreme north Mississippi, where the loess agricultural belt extends farther eastward, has skewed the data along the entire outcrop of the middle Claiborne. While the correlation of agricultural use to higher arsenic values appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. Regionally high arsenic values are associated with the upper Cretaceous across the southeastern U. S.

Plate 4
Arsenic (As) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and geochemical median values within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 5). Higher levels of arsenic seem to be strongly associated with agricultural regions of the state.

Plate 5



Copper (Cu)

Copper, a reddish-brown metal, occurs naturally in sulfide or oxide mineral deposits and is relatively abundant in the earth's crust. It is malleable, ductile, and an exceptional conductor of electricity and heat. The amount of copper present in stream sediment and soil is dependent upon the composition of the parent material, distance from natural ore bodies and/or manmade air emission sources. Copper is considered an essential nutrient in small amounts and is required in the growth process of living organisms. In humans, copper aids in the production of blood hemoglobin. In plants, it is particularly essential in seed production, disease resistance, and aids in the regulation of water intake. However, excessive amounts of copper intake are toxic to living organisms.

Copper is a commercially essential element with extensive use in a wide assortment of products. It is used in all sorts of electrical applications, making textiles, marine paints, plumbing fixtures, coins, and cooking utensils. Copper compounds are commonly used in pest control, photography, medicine, and water treatment/disinfection, as inorganic dyes, as feed additives, as seed disinfectants, as foliage sprays, fertilizers, as antifouling agents. Copper is extremely toxic to fungi and algae and is widely utilized as a fungicide, algicide, and preservative for wood, leather, and fabrics.

Copper typically enters the environment through the mining of copper or other metals, and from industrial sites that manufacture or utilize metallic copper or copper compounds. It may also accumulate via domestic waste water, combustion of fossil fuels and wastes, wood and phosphate fertilizer production. Natural accumulations can result from decaying vegetation, volcanoes, forest fires, or sea spray. Long term use of copper compounds, such as copper sulfate fungicides, for disease control in fruits, vegetables, and ornamental plants could be the source of higher copper concentrations associated with agricultural regions.

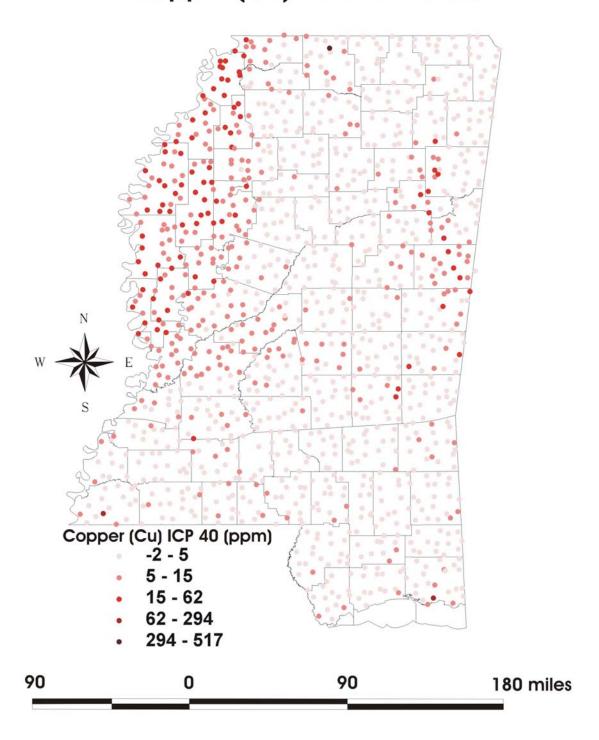
Copper does not break down in the environment. It is insoluble in water and very resistant to corrosion. Copper compounds have widely varying chemical properties and differ from that of the free metal. In these compounds, copper occurs as either copper (I) or copper (II) ions. The free copper (II) ion is potentially very toxic to aquatic life, both acutely and chronically. Its toxicity decreases with high concentrations of dissolved organic compounds and suspended solids, and increases with decreasing water hardness and dissolved oxygen concentration. Copper toxicity is also influenced by pH and alkalinity. In general, simple copper (I) compounds (cuprous compounds) are unstable in water and are quite readily oxidized to copper (II) compounds (cupric compounds). However, cuprous compounds like copper chloride and copper cyanide are stable and insoluble in water. There are numerous cupric compounds and many of them are water soluble. In addition, these ions can combine with a wide variety of dissolved organic compounds. Copper compounds dissolved in water rapidly bind to suspended particles. Copper in soil tends to become strongly fixed to organic material and minerals and reducing its toxicity. Copper is not typically a threat to enter groundwater. Airborne copper particles emitted from smelters and ore processing plants settle to the ground by gravity, and facilitated by precipitation.

Notably, the areas with the highest copper concentrations in Mississippi appear to be associated with the agricultural areas of the Black Prairie, the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas

are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 6) is a point map of sample locations along with corresponding colors that relate to elemental concentration. The (-) sign in the legend should be interpreted as (less than), where 2 ppm is the lower detection limit for copper.

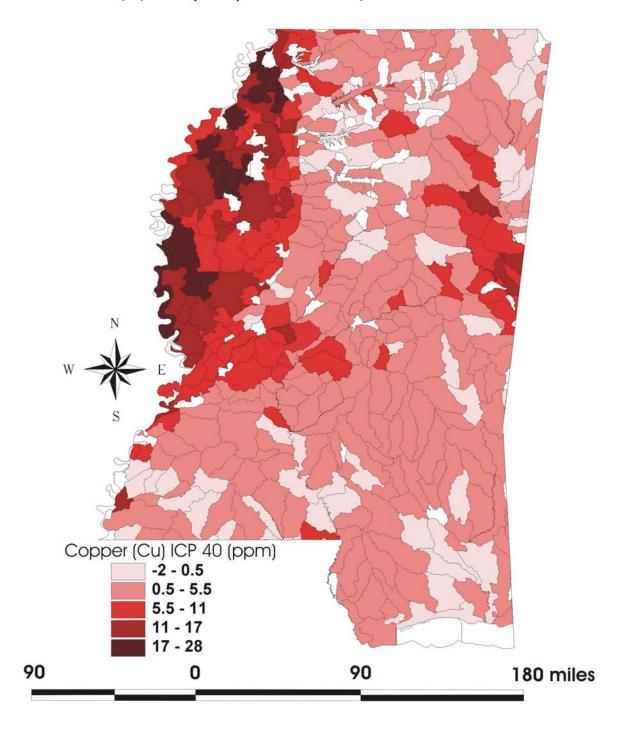
Plate 6

Copper (Cu) Natural Breaks



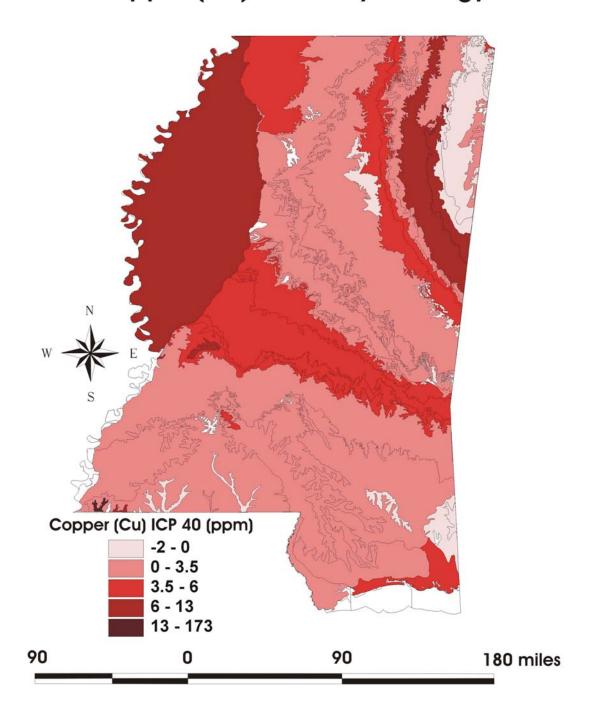
The following derivative map (Plate 7) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for copper. The (-) sign in the legend should be interpreted as (less than), where 2 ppm is the lower detection limit for copper. **Plate 7**

Copper (Cu) Values By Watershed



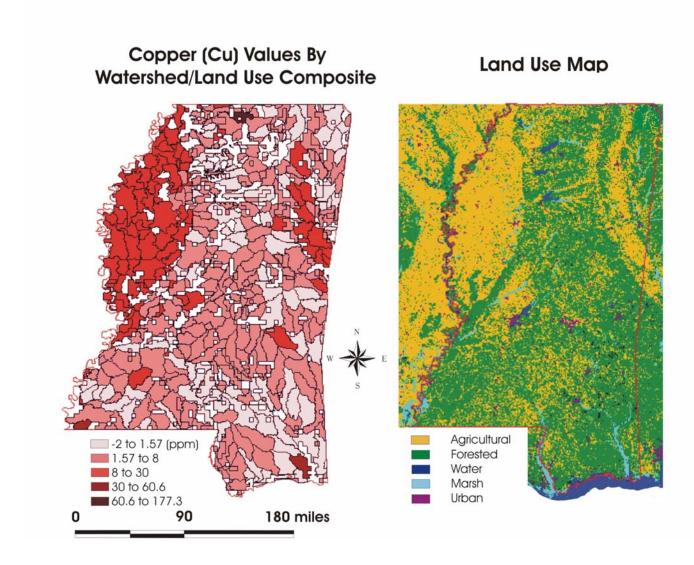
The following derivative map (Plate 8) is based on median geochemical values within a particular geologic unit. The Mississippi River Alluvial Plain, the Jackson Group, and upper Cretaceous units all reflect higher values for copper. These geologic units also coincide with the same high use agricultural areas mentioned previously. Interestingly, the middle Claiborne in extreme northwestern Mississippi is shown to have a relatively high copper value. Some high copper values are evident on the point map near the Tennessee state line in Desoto County. It is likely that this region, where the loess agricultural belt extends farther eastward, has skewed the data to include that polygon mapped as middle Claiborne (Kosciusko Fm.). While the correlation of agricultural use to higher copper values appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. Regionally high copper values are associated with the upper Cretaceous across the southeastern U. S.

Copper (Cu) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and median geochemical values (from ICP 40) within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 9). Higher levels of copper seem to be strongly associated with agricultural regions of the state.

Plate 9



Mercury (Hg)

Mercury is a naturally occurring metal which takes several forms. Metallic mercury is a shiny, silver-white, odorless liquid. When heated, it becomes a colorless, odorless gas. Elemental mercury is stable, and excellent conductor of electricity, and will form alloys with most other metals. It is unsoluble in water, but soluble in fats and oils. Metallic mercury is used in the production of chlorine gas and caustic soda. It is also used in thermometers, dental fillings, floodlights, and batteries. When mercury combines with other elements, such as chlorine, sulfur, or oxygen, it forms inorganic compounds, typically as white powders or crystals (i.e. mercuric chloride). Inorganic mercury typically enters the air from the mining of ore deposits, the burning of coal and waste, and from manufacturing plants. It typically enters water and soil via natural deposits, disposal of wastes in landfills and sewage, and volcanic activity. Mercuric chloride is soluble in water and most organic solvents.

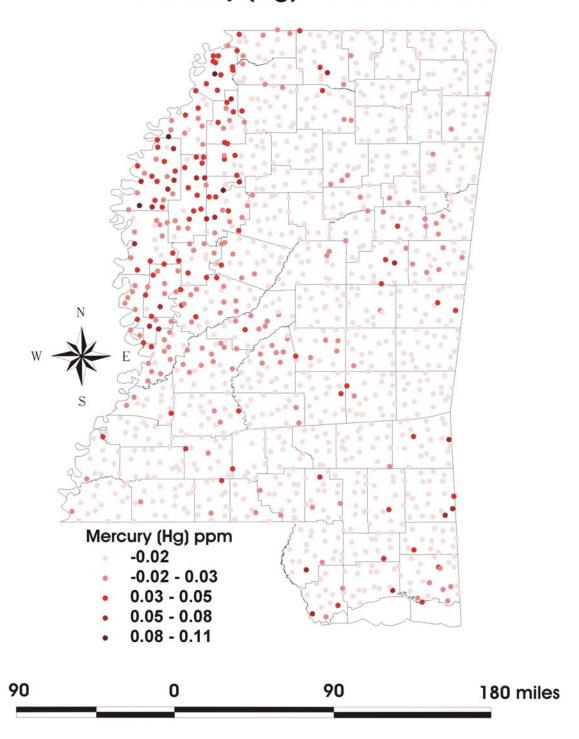
Mercury may also combine with carbon to form organic mercury compounds. The most common type, methyl mercury, is primarily created by bacteria in the soil or water. It is insoluble in water. Increased mercury in the environment can enhance the amount of methyl mercury created by these tiny organisms. Methyl mercury builds up in the tissues of fish, leading to potentially high levels in the larger and older populations.

Historically, mercury was used in agricultural chemicals as a pesticide, fungicide, and mildewcide. The use of mercury-containing pesticides was discontinued in 1969 for food related use. All United States pesticide registrations were canceled in as of early 1995. Former mercury-based products which are no longer permitted include turf fungicide, mildewcide for fresh cut wood, latex paint fungicide/preservative, and outdoor fabric treatment. Nevertheless, significant accumulations of mercury compounds may still be present on farms and golf courses. Mercury and mercury compounds are long lasting in the environment, being highly and acutely toxic to aquatic life. High chronic toxicity to aquatic life is also a concern. Consumption of fish contaminated with mercury can cause poisoning in humans.

Notably, the areas with the highest mercury concentrations in Mississippi appear to be associated with the agricultural areas of the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 10) is a point map of sample locations along with corresponding colors that relate to elemental concentration. The (-) sign in the legend should be interpreted as (less than), where 0.02 ppm is the lower detection limit for arsenic.

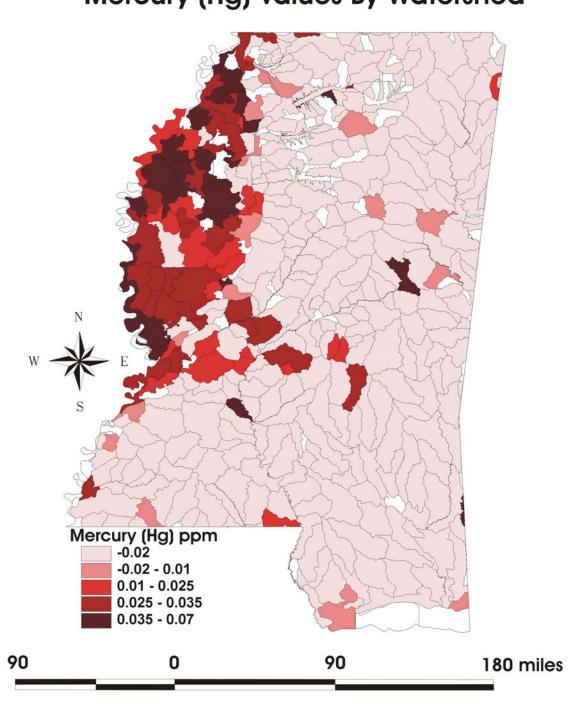
Plate 10

Mercury (Hg) Natural Breaks



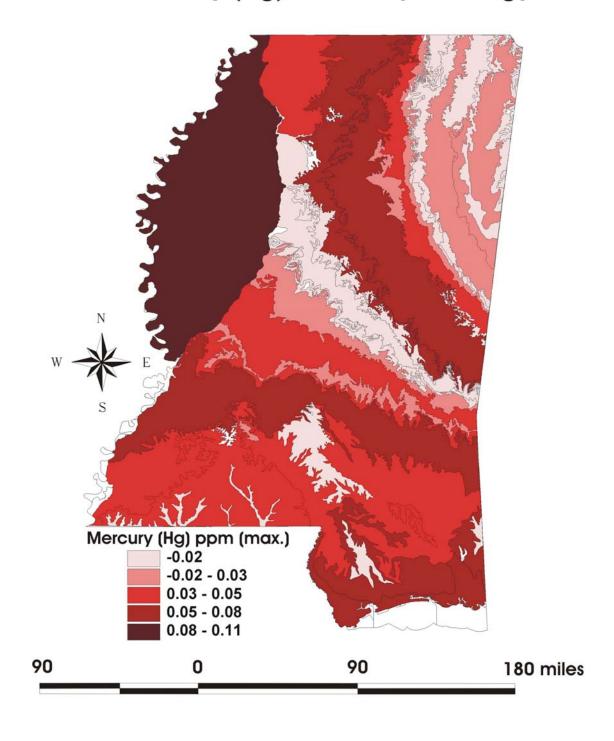
The following derivative map (Plate 11) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for mercury.

Mercury (Hg) Values By Watershed



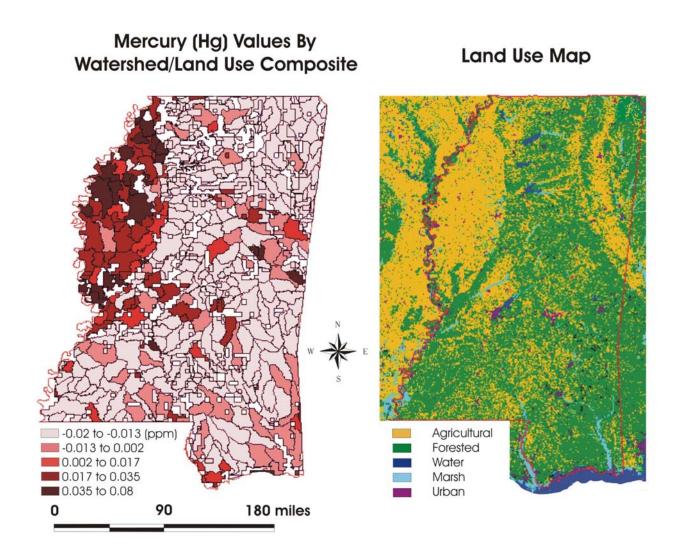
The following derivative map (Plate 12) is based on maximum geochemical values within a particular geologic unit. The Jackson Group, Mississippi River Alluvial Plain, and the northwestern portion of the Kosciusko Fm./Loess belt reflect higher values for mercury. These geologic units also coincide with the same high use agricultural areas mentioned previously. The Black Prairie agricultural belt is only moderately high in comparison. The remainder of the state portrays a number of units with relatively high mercury values. The point map for mercury (Plate 10) shows that some samples with "high" mercury values exist sporadically and without any obvious association. These higher values, particularly in south Mississippi, likely result from airborne deposition of mercury. Much of the mercury in Mississippi stream sediment and soil is likely derived from either agricultural activities or from airborne contamination.

Plate 12 Mercury (Hg) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and median geochemical values within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 13). Higher levels of mercury seem to be strongly associated with agricultural regions of the state.

Plate 13



Lead (Pb)

Lead is a naturally occurring dense, malleable metal found in small amounts in the earth's crust. Lead can be found in all parts of our environment. Much of it, however, comes from human activities such as mining, manufacturing, and burning fossil fuels. Lead has varied industrial uses, including, battery and ammunition production, metal products such as solder and pipes, and devices to shield X-rays. Due to health concerns, lead use in gasoline, paints and ceramic products, caulking, and pipe solder has been significantly lessened in recent years. Lead arsenate was a commonly used pesticide prior to World War II, and could be the source of higher lead concentrations associated with agricultural regions.

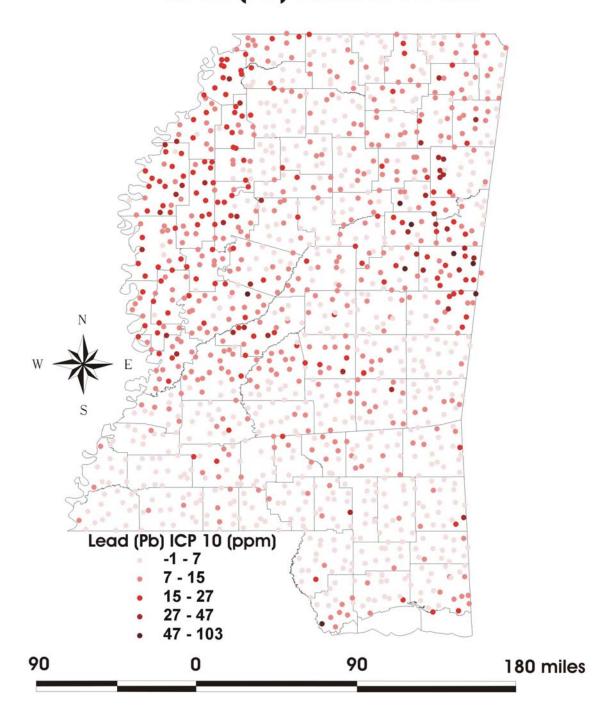
Lead does not break down in the environment, although, lead compounds may be modified by sunlight, air, and water. Lead is not soluble in water; however, it may react with impurities in water to create soluble lead compounds. When lead is released into the air, it may travel long distances before settling to the ground. Once lead falls onto soil, it generally affixes to soil particles. Transfer of lead from soil into groundwater depends upon the type of lead compound in addition to the characteristics of the soil. Lead is very insoluble in soil and is not readily taken up by plants. Much of the lead associated with inner-city soils is derived from accumulations of lead-based paint debris emanating from older structures. High intensity transportation areas may also have high lead accumulations resulting from automobile emissions and subsequent atmospheric deposition.

Lead enters the human food-chain largely through direct ingestion of tainted soil or lead-containing substances. The immediate consequence of lead exposure can cause death in animals, birds or fish; also death or low growth rate in plants. Chronic effects on animal life may be reduced lifespan, reproductive difficulties, and changes in behavior or appearance. Because lead does not break down and is highly persistent in water, it is expected that fish tissues from polluted waters will contain lead. Lead is more toxic in soft water.

Notably, the areas with the highest lead concentrations in Mississippi appear to be associated with the agricultural areas of the Black Prairie, the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 14) is a point map of sample locations along with corresponding colors that relate to elemental concentration.

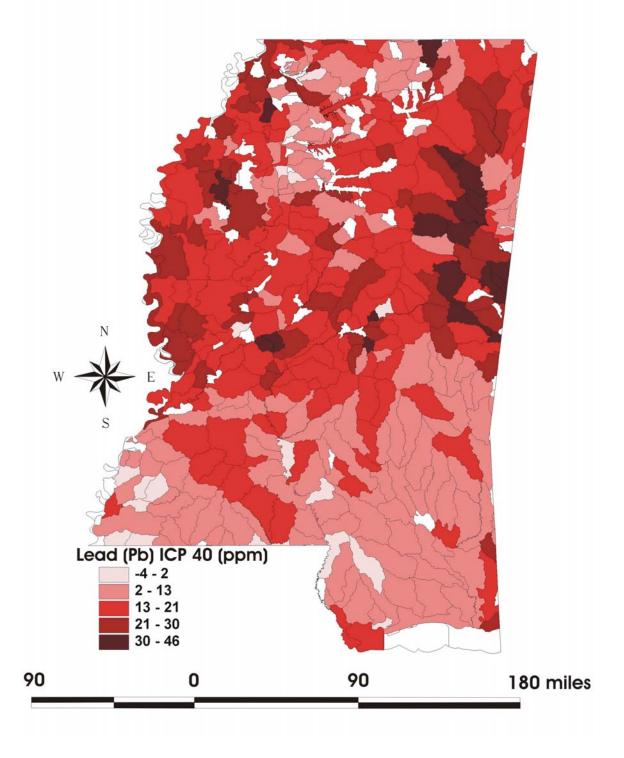
Plate 14

Lead (Pb) Natural Breaks



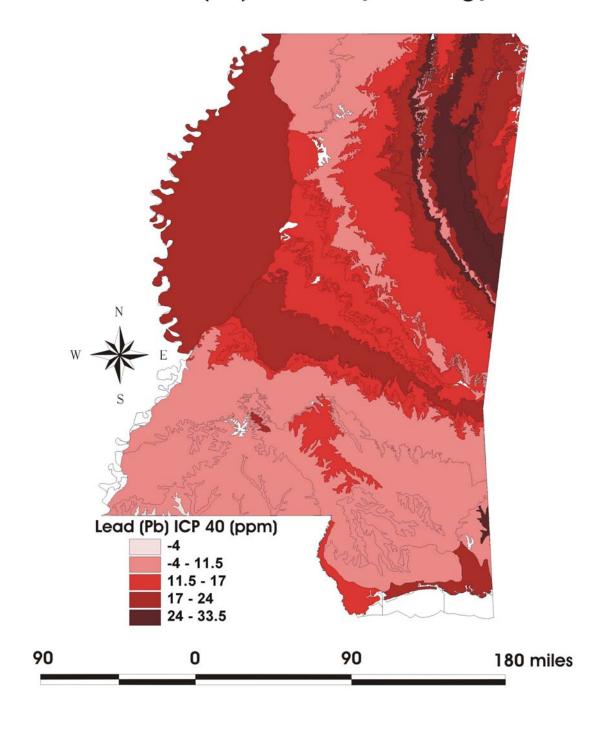
The following derivative map (Plate 15) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for lead.

Lead (Pb) Values By Watershed



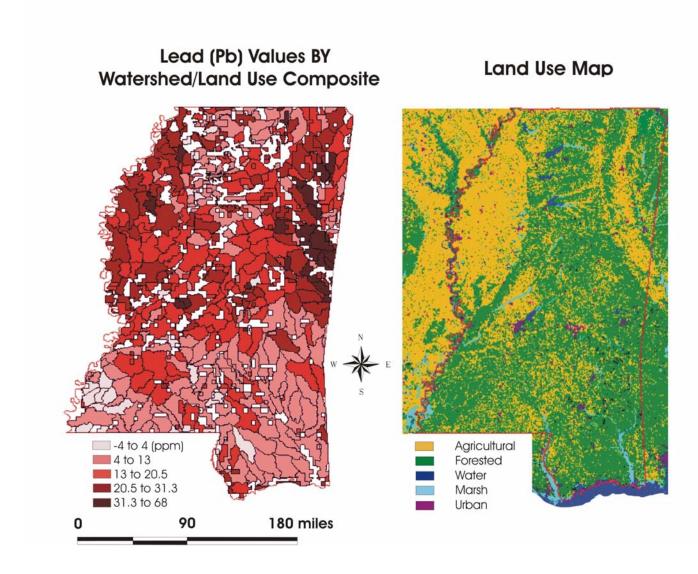
The following derivative map (Plate 16) is based on median geochemical values within a particular geologic unit. The Mississippi River Alluvial Plain, the Jackson Group, and upper Cretaceous units all reflect higher values for lead. These geologic units also coincide with the same high use agricultural areas mentioned previously. The remainder of the state portrays a number of units with relatively high lead values. The point map for lead (Plate 14) shows that some samples with "high" lead values exist sporadically and without any obvious association. These higher values, particularly in south central Mississippi, may result from airborne deposition of lead. In addition, there are "high" lead levels noted with the Coastal Deposits. Prominent soil sampling in this region likely plays a role in the higher relative statewide values. Also, there are a number of industrial sites along the coast which could be a factor. While the correlation of agricultural use to higher lead values appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values.

Plate 16 Lead (Pb) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and median geochemical values (from 1CP 40) within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 17). Higher levels of lead seem to be strongly associated with agricultural regions of the state.

Plate 17



Selenium (Se)

Selenium occurs naturally and widely, albeit rarely, in the earth's crust and is found naturally in igneous rocks, volcanic sulfur deposits, hydrothermal deposits, copper deposits, and in sedimentary rocks such as sandstone, carbonaceous siltstones, phosphorite rocks, limestone, iron, coal and some crude oil deposits. It is a metalloid, possessing both metallic and non-metallic properties, and may be a gray, red or black solid. The most stable form is gray and metallic. The earth's crust is said to have an average selenium concentration of 0.03 of 0.08 ppm. Conspicuously higher accumulations (2 to 10 ppm) have been noted in Cretaceous marine shales of West and Midwestern states. Small amounts of selenium are found in many sulfide ores, such as those of iron, copper, silver, or lead, typically occurring as selenide. The commercial supply of selenium is obtained primarily as a byproduct of ore processing (from the anode mud of copper refineries and the mud from the lead chambers of sulfuric acid plants). Selenium has a wide variety of commercial uses: essential component in animal nutrition; constituent in dandruff shampoos, treatments for fungal infection, and other medicinal therapies; used in manufacture of ruby-colored glasses and enamels, photoelectric cells, resistors, photographic emulsions, stainless steel, pigments, metal alloys, rubber, textiles, petroleum products, insecticides, fungicides, and fertilizers.

In its natural state as an element, selenium cannot be destroyed; however, selenium does have the capacity to change form and is very chemically adaptable. Selenium combines with both metals and non-metals, directly and hydrochemically; forms both organic and inorganic compounds; is an oxidant as well as a reductant (an important factor in soil formation). Elemental or free selenium is considered nontoxic and is an essential nutritional trace element; however, hydrogen selenide and other selenium compounds are extremely toxic, and resemble arsenic in their physiological reactions. Hydrogen selenide at a concentration of 1.5 ppm is intolerable to man. Behaving chemically like sulfur and tellurium, selenium quickly becomes toxic in higher doses; five time more poisonous than arsenic. For instance, selenium is required and beneficial in the diet of cattle at a level of no less than 0.4 ppm but can be toxic at levels greater than approximately 4 ppm. Not only does selenium dosage and accumulation have a narrow range between safety and danger, but the range of optimal beneficial action is very narrow and still has not been determined with certainty.

Selenium may also be released into the environment through human activities. Anthropogenic activities such as mining, smelting, the burning of coal and oil, and fertilizer application are prime contributors to local selenium deposition in soil or water; subsequently absorbed by plants or becoming airborne with dust particles. Selenium is the most strongly enriched element in coal, being present as an organoselenium compound, a chelated species, or as an adsorbed element. Selenium typically becomes airborne by way of coal and oil combustion in the form of selenium dioxide. Elemental or free selenium is virtually insoluble in water; however, compounds such as selenium dioxide and selenium trioxide dissolve in water to form selenious acid and selenic acid, respectively, and the corresponding salts are selenite and selenate. These forms of water-soluble selenium are highly toxic; easily leached from the soil and available to plants. Selenium in soil remains fairly immobile unless it reacts with oxygen. Selenium in an immobile state and undissolved in water is of less risk to organisms. When selenium occurs in alkaline soils (such as those of the Western U.S., the site of the most recent

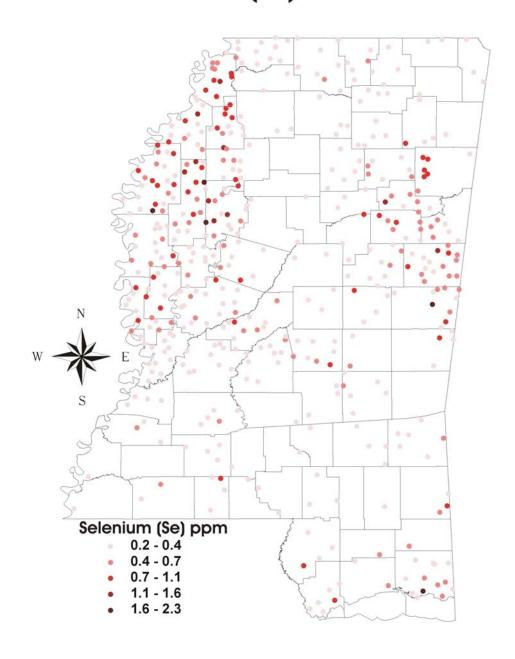
volcanic activity) and becomes oxidized as selenate, it becomes water-soluble. These toxic, mobile forms of selenium are also brought about through industrial or agricultural activities. Agricultural activity tends to increase the selenium content in soil and can also increase selenium concentrations in surface water, whereby the selenium is distributed along irrigation drainage-ways. The rate at which mobile selenium moves through the soil is dependent upon the interaction with other compounds, soil temperature, moisture, organic matter content, microbial activity, the concentration of water-soluble selenium, and the season of the year. Soil bacteria and fungi also play a role in the oxidation of elemental selenium into selenite and selenate. Increased solubility, of course facilitates their uptake by certain plants. Plants grown in selenium-rich soils, such as locoweed, can cause serious effects on animals feeding on the plants. In acid soils, whether selenium occurs as a trace element or as selenide (bound to other metals), the selenium is still toxic, but being bound to other metals, it is not actively available to plants to work its way into the food chain.

Presence in Soil: Background levels in eastern U.S. soils are typically 0.1-3.9 ppm. The concentration of selenium in most normal soils is estimated to be 0.2 ppm (Rosenfeld and Beath 1964). In short, the chances of exposure to selenium compounds are greatly enhanced when selenium is in a mobile state. Rainy regions are less likely to experience the problem from naturally occurring selenium because selenium and other salts have been flushed from the soil profile. Mammals and aquatic life experience high short term toxic effects to selenium and selenium compounds; whereas birds face moderate short term toxic effects. Selenium can be expected to bioaccumulate in fish where water levels of selenium are elevated.

The original source of selenium was probably volcanic activity; selenium is frequently associated with volcanic deposits and coincident with sulfur emissions. However, certain volcanic regions are characterized by selenium deficiencies, such as the recent volcanic deposits of the Pacific Northwest and Tertiary volcanic rocks in New Mexico and Arizona. Coastal deposits derived from highly weathered and leached parent material are likewise typically selenium deficient. Also, selenium deficiencies have been noted in soils of the Northeastern states, as the associated underlying Paleozoic sedimentary formations are likewise deprived. These areas also tend to correspond to areas where selenium-deficiency disorders tend to occur.

Notably, the areas with the highest selenium concentrations in Mississippi appear to be associated with the agricultural areas of the Black Prairie, the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 18) is a point map of sample locations along with corresponding colors that relate to elemental concentration. Sample locations with values below the detection limit for selenium (0.2 ppm) are not depicted.

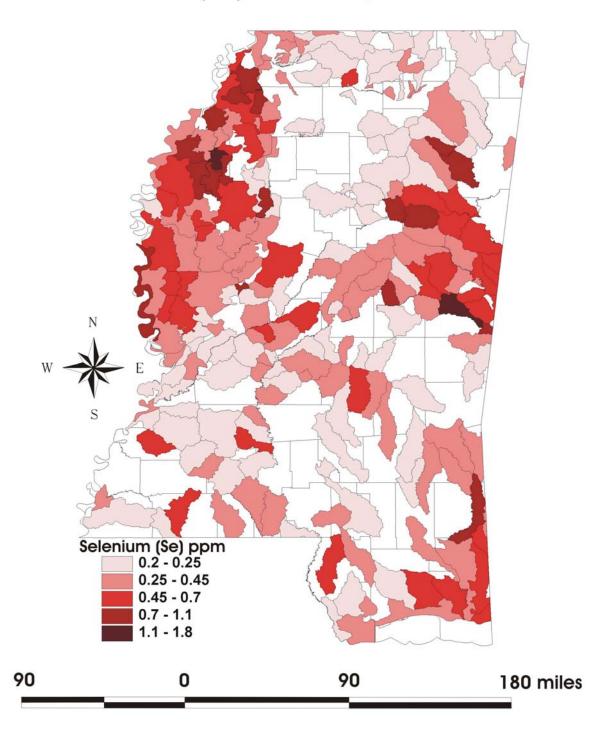
Plate 18
Selenium (Se) Natural Breaks





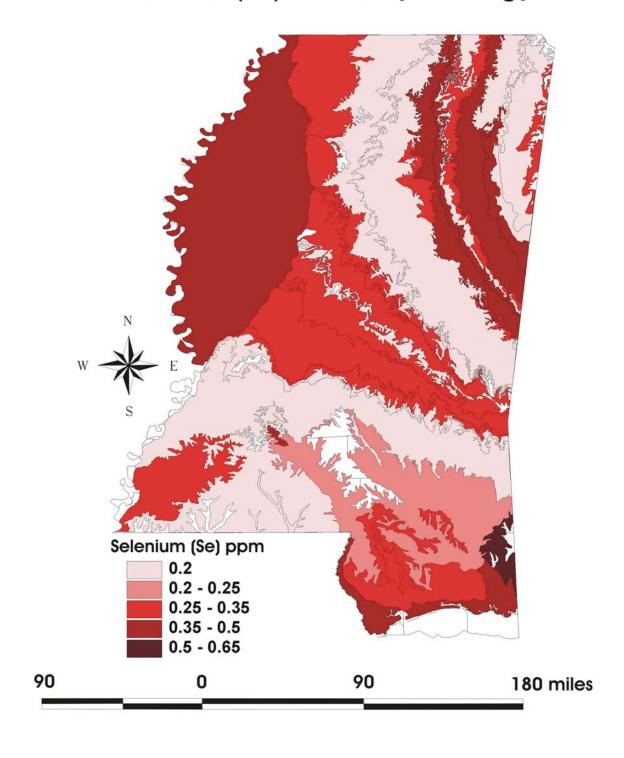
The following derivative map (Plate 19) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for selenium. Watershed polygons which contain sample locations with geochemical values below detectable limits for selenium are not depicted. **Plate 19**

Selenium (Se) Values By Watershed



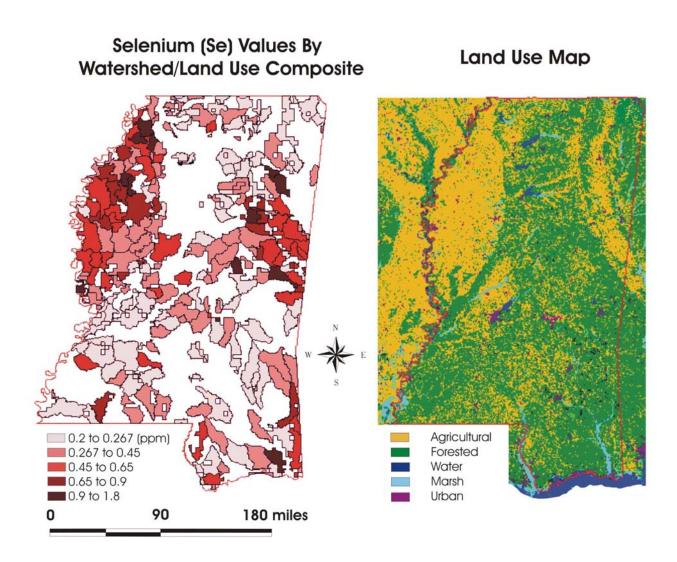
The following derivative map (Plate 20) is based on median geochemical values within a particular geologic unit. The Mississippi River Alluvial Plain, the Jackson Group, and upper Cretaceous units all reflect higher values for selenium. These geologic units also coincide with the same high use agricultural areas mentioned previously. Interestingly, the middle Claiborne is shown to have a relatively high selenium value. Some high arsenic values are evident on the point map near the Tennessee state line in Desoto County. It is likely that this region of extreme north Mississippi, where the loess agricultural belt extends farther eastward, has skewed the data along the entire outcrop of the middle Claiborne. The point map for selenium (Plate 18) shows that some samples with "high" selenium values exist sporadically and without any obvious association. These higher values, particularly in south central Mississippi, may result from airborne deposition of selenium. In addition, there are "high" selenium levels noted with the Coastal Deposits. Prominent soil sampling in this region likely plays a role in the higher relative statewide values. Also, there are a number of industrial sites along the coast which could be a factor. While the correlation of agricultural use to higher selenium values appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. Geologic polygons which contain sample locations with geochemical values below detectable limits for selenium are shown in white.

Selenium (Se) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and median geochemical values within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 21). Higher levels of selenium seem to be strongly associated with agricultural regions of the state. Polygons which contain sample locations with geochemical values below detectable limits for selenium are not depicted and appear as white space.

Plate 21



Zinc (Zn)

Zinc, a bluish-white, lustrous metal, is relatively abundant and natural levels of zinc are found in rocks, soil, air, plants, animals, and humans. Natural levels of zinc are present in food and water, and small amounts are regularly ingested. Zinc (in trace quantities) is considered essential for human health. Zinc is easily obtained from its ores. The main minerals are sulfides (sphalerite, wurtzite). Zinc forms many alloys, for example brass (an alloy with copper). Numerous zinc compounds have a wide variety of uses. For instance, zinc pyrithione is a chemical compound used to inhibit fungi, bacteria, and algae in the manufacture of plastics, latexes, and polymers. Zinc phosphide is an inorganic chemical pesticide used to control rats, mice, gophers, etc. It is also uses as a tracking powder for the control of house mice, as a stomach poison for mosquito larvae and agricultural pests. It is used on crop areas and on non-crop areas including lawns, golf courses, highway medians, and areas adjacent to wetlands. It may be prepared as a grain, scrap bait or paste. Zinc phosphide is highly toxic to wild birds and freshwater fish. It is also toxic to non-target mammals. Soil acidity tends to break the compound down liberating phosphine a highly toxic gas. There is a potential for movement of this compound into adjacent, slightly acidic waters, where it can endanger fish populations. Zinc sulfate has numerous commercial applications including fertilizer ingredient, herbicide, feed supplement, dietary supplement, soil treatment on lawns, bacteriological pathogen treatment in sewage, and is used in preservatives, glue, and textile production. Zinc minerals contain cadmium as a common impurity which will be released when zinc is refined. Cadmium is a cancer-causing agent and thus much more harmful than zinc itself. Some imported zinc sulfate has been found in recent years to be contaminated with cadmium, which would increase toxicity exposure to farm workers and farmlands.

Some zinc is released into the environment by natural processes (volcanic emissions, forest fires), however, zinc concentrations are increasing unnaturally through anthropogenic activities such as mining, coal and waste combustion, steel processing, and excessive use of zinc compounds in products applied to land, like zinc fertilizers and herbicides. Because the world's zinc production is rising, zinc levels in the environment will likely continue to increase. Zinc can be transported as particles released into the atmosphere or as dissolved compounds in natural waters. Zinc attaches to dust particles in the air which settle to the ground or are taken out of the air by rain. Zinc attaches to soil and sediment particles and most of the zinc will stay bound. Some zinc will move into the ground water and into lakes, streams, and rivers where it combines with other organic or inorganic matter. Most of the zinc in bodies of water settles to the bottom. However, a small amount may remain either dissolved in water or as finely suspended particles. Because of large quantities of zinc in inadequately treated industrial wastewater, surface water is widely polluted with zinc. Streams that receive zinc-tainted water may see increased acidity levels and tend to precipitate zinc-polluted sludge along their banks. Additionally, fish in zinc-contaminated waterways can bio-accumulate zinc in their bodies, which in turn can bio-magnify up the food chain.

Zinc is insoluble in water but reacts readily with non-oxidizing acids, forming zinc cations and releasing hydrogen. It also dissolves in strong bases. Zinc ions found in

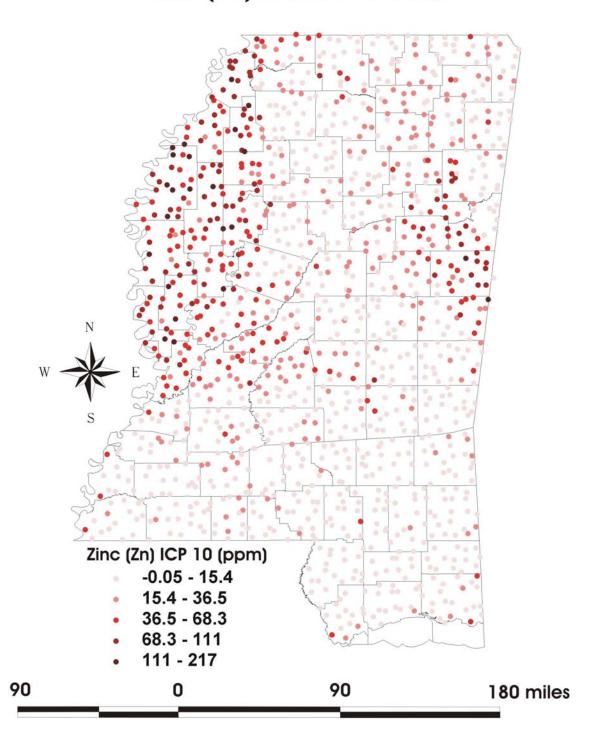
aquatic environments are in the (II) oxidation state. It is rarely encountered as the free zinc (II) ion due to its strong tendency to form complexes with inorganic and organic compounds freely available in nature. Some zinc compounds, such as zinc sulfate and zinc chloride, are readily soluble in water. Others, such as zinc oxide and zinc sulfide, are virtually insoluble in water. The toxicity of zinc in water is influenced by water hardness and pH, with lower toxicity encountered in waters with higher water hardness and lower pH, and vice versa. Generally, zinc and its salts have high acute and chronic toxicity to aquatic life in polluted waters. Fish can accumulate zinc moderately. Insufficient data are available to evaluate or predict the short term and the long term effects of zinc and its compounds to plants, birds, or land animals. Corrosion of galvanized structures can release zinc into soil and water.

Sizeable quantities of zinc can be found in soils. Farmland soil polluted with zinc can affect the health of animals if they take in excessive concentrations. Zinc is not only a threat to farm animals, but it can also be dangerous to plant species, where by the level of zinc uptake surpasses what their system can manage. Also, water-soluble zinc compounds in soils can contaminate groundwater.

The toxicity of zinc and many zinc compounds to plants and animals is generally low compared with the significance of zinc deficiency. Soils with an excessive zinc burden, e.g. in the vicinity of zinc smelters, can be toxic to plants. Soil pH is one factor that influences zinc availability to plants. Bioavailability increases with lower pH values, but wash-out is also more likely under more acidic conditions. Plant population is diminished in areas with zinc rich soils and high levels of zinc can be a significant threat to farmland production. On zinc-rich soils only a limited number of plants have a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Nevertheless, some areas continue farming practices where manure containing zinc is spread as fertilizer. Further, zinc can adversely affect biological activity in soils, negatively influencing the activity of micro-organisms and earthworms, and slowing down the decomposition of organic matter.

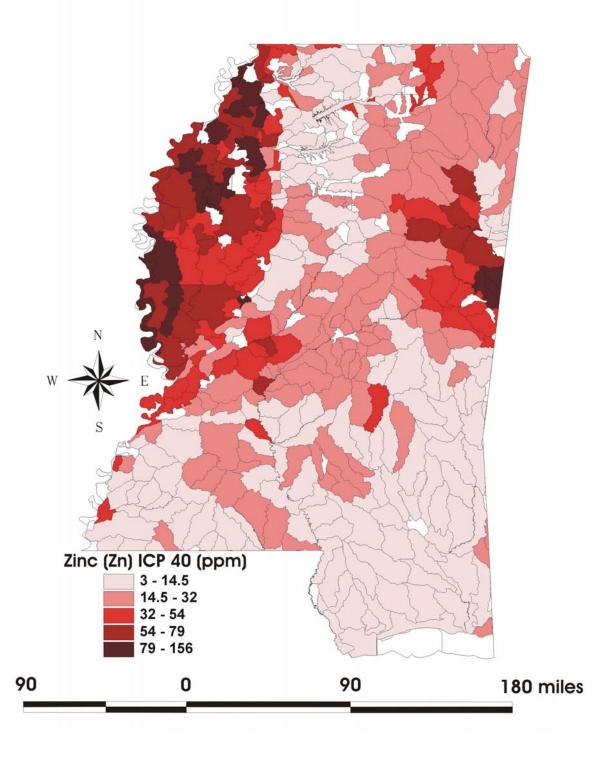
Notably, the areas with the highest zinc concentrations in Mississippi appear to be associated with the agricultural areas of the Black Prairie, the Delta region, and the Jackson Prairie. While this correlation appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values. The map below (Plate 22) is a point map of sample locations along with corresponding colors that relate to elemental concentration. The (-) sign in the legend should be interpreted as (less than), where 0.05 ppm is the lower detection limit for zinc.

Zinc (Zn) Natural Breaks



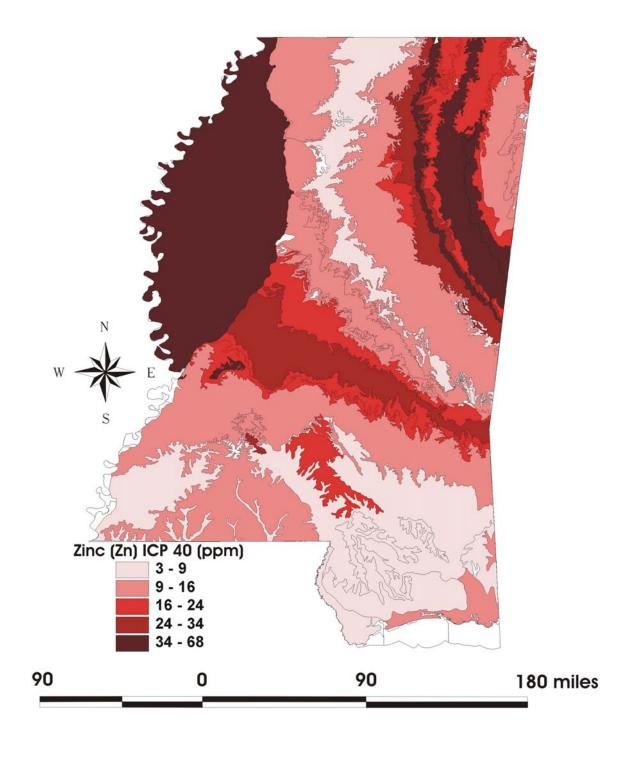
The following derivative map (Plate 23) is based on median geochemical values within a particular watershed. In general, watersheds located within high agricultural use areas appear to reflect higher values for zinc.

Plate 23
Zinc (Zn) Values By Watershed



The following derivative map (Plate 24) is based on median geochemical values within a particular geologic unit. The Mississippi River Alluvial Plain, the Jackson Group, and upper Cretaceous units all reflect higher values for zinc. These geologic units also coincide with the same high use agricultural areas mentioned previously. The point map for zinc (Plate 22) shows that some samples with "high" zinc values exist sporadically and without any obvious association. These higher values, particularly in south Mississippi, may result from airborne deposition of zinc. While the correlation of agricultural use to higher zinc values appears sound, it should be noted that these areas are also defined by distinctive geologic provinces, and natural geologic conditions could play a role in elevated values.

Zinc (Zn) Values By Geology



Efforts to produce a derivative geochemical map with land use polygons were problematic and results were flawed. In an attempt to relate land use relationships to geochemistry, a composite watershed/land use map was created by Paul Schruben (USGS) and median geochemical values (from ICP 40) within particular watershed/land use polygons are depicted. It is useful to compare this map to a simplified land use map of Mississippi (Plate 25). Higher levels of zinc seem to be strongly associated with agricultural regions of the state. The (-) sign in the legend should be interpreted as (less than), where 2 ppm is the lower detection limit for zinc.

The final figure, Plate 26, utilizes sum values of the six toxic elements discussed in this atlas. The concentration values are depicted in both a point map and watershed map. Similar associations and patterns are developed and the strong association of elevated toxic elements to agricultural regions is reinforced. The (-) sign in the legend should be interpreted as (less than), where 16 ppm is the lower detection limit for the sum elements.

Plate 25

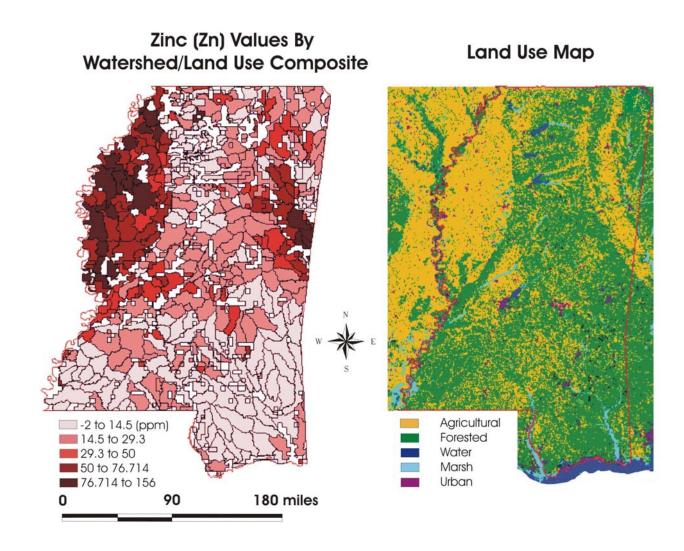
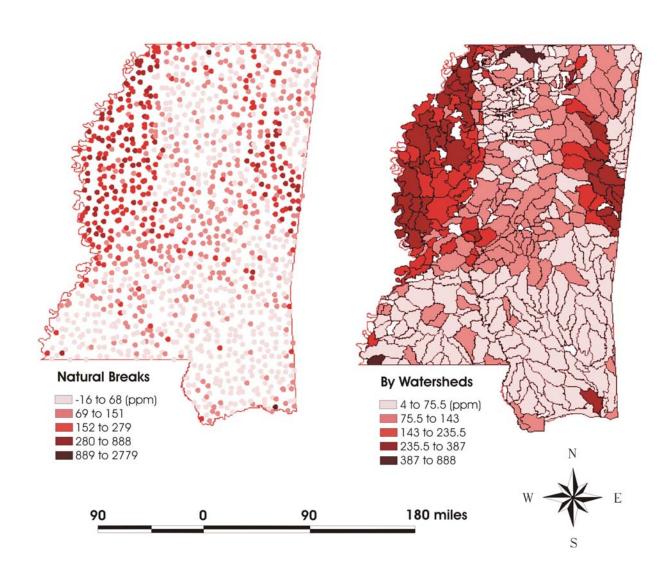


Plate 26
Toxic Elements Sum Maps for As, Se, Cu, Pb, and Zn



*This atlas was updated/revised on April 5, 2005

Acknowledgements

U. S. Geological Survey personnel, cooperative partners with this project, provided crucial analytical funding and technical expertise. Andrew E. Grosz developed the project concept and design, developed and supervised the sampling protocols and field methods, and offered outstanding leadership. Paul G. Schruben provided crucial GIS support. Jeffrey N. Grossman developed the database design, processed the data; developed geochemical mapping methods and computer methods in support of geochemical sampling. This project should stand as a shining example of successful federal and state government cooperation.

Sources of information used in preparing this atlas

Bauer, F., 1997, Selenium and Soils in the Western United States, Electronic Green Journal, Issue 7, University of Wyoming

Libraries, web publication - http://egj.lib.uidaho.edu/egj07/

Gough, L. P., 1993, Understanding Our Fragile Environment--Lessons from Geochemical Studies, Circular 1105, U. S.

Geological Survey, 34 p.

Gough, L. P., Severson, R. C., and Shacklette, H. T., 1988, Element Concentrations in Soils and Other Surficial Materials of

Alaska, Professional Paper 1458, U. S. Geological Survey, 53 p.

Grossman, J. N., Grosz, A. E, Schweitzer, P. N., and Schruben, P. G., The National Geochemical Data Base, Open-File

Report 2004-1001, Version 1.0, U. S. Geological Survey, web publication – http://tin.er.usgs.gov/geochem/doc/home.htm

Shacklette, H. T. and Boerngen, J. G., 1894, Element Concentrations in Soils and Other Surficial Materials of the

Conterminous United States, Professional Paper 1270, U. S. Geological Survey, 105 p. Thompson, D. E., A. E. Grosz, J. M. McNeal and J. N. Grossman, 1998, Surface

geochemistry of Mississippi to be surveyed: Mississippi Geology v. 19, no. 2, p. 13-19.

Thompson D. E., A. E. Grosz, P. G. Schruben and J. N. Grossman, 2002, Solid-phase geochemical survey of the State of Mississippi; on the nature and distribution of As, Se, Hg, Cu, Pb, and Zn in stream sediments and soils [abs.]: Journal of the Mississippi Academy of Sciences, v. 47, no. 1, p. 42.

Other World Wide Web Sources

Frequently Asked Questions about the Environment, U. S. Geological Survey, Compiled by the Geologic Inquiries Group,

http://geology.er.usgs.gov/eastern/environment/environ.html

Department of Health and Human Services, Centers for Disease Control and Prevention, National Center for Environmental Health, Agency for Toxic Substances and Disease Registry/ NCEH/ATSDR, http://www.atsdr.cdc.gov

Lenntech Periodic Table, http://www.lenntech.com/periodic-chart.htm

The Australian Government Department of the Environment and Heritage (DEH), http://www.deh.gov.au/

U.S. Environmental Protection Agency, http://www.epa.gov

