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**Geochemical Maps of Copper, Lead, and Zinc,
Upper Arkansas River Drainage Basin, Colorado**

By

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INTRODUCTION

Historic mining activity in and around Leadville, Colorado, has contributed to the environmental degradation of the Arkansas River and its riparian habitat zone. High concentrations of several ore metals have been reported in sediments of the Pueblo Reservoir and attributed to contamination from mining in Leadville, 235 kilometers upstream (Callender and others, 1989). However, Leadville is not the only source of metal contamination in the drainage basin. Several other mining districts and mineralized areas also contribute sediments containing elevated concentrations of trace and heavy metals into the Arkansas River.

In 1993, the U.S. Geological Survey (USGS) began a study of trace-element and heavy-metal distribution in the Arkansas River drainage basin of Lake County, Colorado. Samples of active stream sediments and cores of recent sediments were collected to evaluate the contributions and isotopic composition of lead from potential sources near Leadville (Church and others, 1993). Soon after the completion of this study, the USGS began a study of the upper Arkansas River drainage basin, from Leadville to the Pueblo Reservoir, to assess concentrations and sources of trace-element and heavy-metal contamination.

Before establishing a strategy for the collection of new river-sediment samples for the assessment, geochemical maps of the upper Arkansas River drainage basin study area were prepared, based on existing data. Geochemical maps provide an estimate of the baseline concentrations for a specific element over a region at the time the samples were collected. The distribution of a particular element is controlled primarily by the exposed rocks within the mapped area. Mining districts, smelter sites, industrial sources of trace and heavy metals and undisturbed mineralized areas are readily identified on geochemical maps by their elevated metal concentrations within the geologic framework. This report documents the methods used to compile and correct the available geochemical data and gridding and contouring methods used to produce geochemical maps for copper, lead, and zinc in the upper Arkansas River drainage basin study area.

METHODS OF STUDY

The USGS Branch of Geochemistry has developed a National Geochemical Data Base (NGDB) containing analytical and site information for rock, sediment, plant, and water samples (Hoffman and Marsh, 1994). For this study, all geochemical data from stream-sediment samples (referred to hereafter as stream-sediment data), within a rectangular block between 37°00' and 39°30' north latitude and between 104°00' and 106°45' west longitude, were retrieved from the NGDB. This region includes the entire upper Arkansas River drainage basin study area and a margin of at least 15' longitude and latitude around the study area.

The stream-sediment data retrieved from the NGDB can be broadly divided into two types: data from samples collected as part of the National Uranium Resource Evaluation (NURE) program and data from USGS mineral resource assessment studies of federal lands.

NURE Data

The NURE program was established by the U.S. Atomic Energy Commission, now the U.S. Department of Energy, in 1973 to assess uranium resources and to identify favorable areas for detailed uranium exploration throughout the United States (Arendt and others, 1979). Authority was given to four Federal laboratories to conduct geochemical surveys on a 1° x 2° quadrangle basis. The Los Alamos Scientific Laboratory, in Los Alamos, New Mexico, was responsible for the Rocky Mountain states including all of Colorado. Actual sampling within the quadrangles that cover the upper Arkansas River drainage basin was done between March 14, 1976 and October 11, 1979. The NURE stream-sediment samples were analyzed by the Los Alamos Scientific Laboratory using various techniques. Copper and lead were determined by X-ray fluorescence and zinc was determined by neutron activation analysis.

Within the retrieved block are data collected from six NURE Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) quadrangle studies: the Denver quadrangle (Bolivar and others, 1978; Shettel and others, 1981), the Durango quadrangle (Shannon, 1980a), the Leadville quadrangle (Planner and others, 1981), the Montrose quadrangle (Broxton and others, 1979), the Pueblo quadrangle (Shannon, 1978; 1979b), and the Trinidad quadrangle (Morris and others, 1978; Shannon, 1980b). Data from two additional detailed NURE studies also included the Sawatch Range special study (Maassen and others, 1981) and the Tallahassee Creek, Badger Creek, Castle Rock Gulch, and Buffalo Gulch study areas (Shannon, 1979a).

USGS Data

Several USGS mineral-resource assessment studies produced stream-sediment data within the area retrieved. These studies include six Wilderness Study Area (WSA) projects (Buffalo Peaks WSA—Domenico and others, 1984; Fossil Ridge WSA—Adrian, Clark, and others, 1984; Greenhorn Mountain WSA—Toth and others, 1983; Hunter-Fryingpan WSA and Porphyry Mountain WSA—Mosier and others, 1980; and the Sangre de Cristo WSA—Zimbelman and others, 1983; Adrian, Arbogast, and Zimbelman, 1984), the Conterminous United States Mineral Assessment Program (CUSMAP) Pueblo 1° x 2° quadrangle project (Zimbelman and others, 1985), and some unpublished data from the Pando-Tennessee Pass area (H. King, personal commun., 1994).

All of the USGS stream-sediment samples within the area retrieved were collected between 1976 and 1982 and analyzed by multiple-element, semi-quantitative DC-arc optical emission spectrography (OES). Additionally, several samples were also analyzed for selected elements by atomic absorption (AA) methods. For the elements discussed in this report, copper and lead were determined by OES, and zinc was determined by both OES and AA.

Other Data

A literature search found additional studies in the region that are not yet included in the NGDB. These data were not immediately available in a digital form and consequently not used in this study. The data sources are listed in Table 1 as a guide for further data base development and study within the upper Arkansas River drainage basin area.

Table 1: Additional stream-sediment data collected within the region of the upper Arkansas River drainage basin study area, not included in this study.

<u>Project</u>	<u>Estimated additional data</u>	<u>Reference</u>
NURE follow-up - Denver	301 stream sediments	(Hills and others, 1982)
NURE follow-up - Durango	24 stream sediments	(Theis and others, 1981)
NURE follow-up - Leadville	12 stream sediment/soils	(Collins and others, 1982)
NURE follow-up - Montrose	30 stream sediments	(Goodnight and Ludlam, 1981)
NURE follow-up - Pueblo	151 stream sediments	(Dickinson and Hills, 1982)
NURE follow-up - Trinidad	139 stream sediments	(Johnson and others, 1982)
Browns Canyon mineral resources	147 stream sediments	(Lieboldt and others, 1987)
BLM Arkansas Canyon Planning Unit geochemical survey	700 stream sediments	(Weiland and Grauch, 1981)

Data Evaluation

Historically, descriptive sample data from each NURE and USGS project have been entered into a data base from information supplied by the collector and the geochemical data were later added from the laboratory. When the analyses have been completed, a project retrieval is made, the data are examined for errors and the corrected data set is then published as a data release. Unfortunately, these corrections have not always been made to the original data bases. Additionally, an incomplete data base reformatting process has added many other problems to the NURE portion of the National Geochemical Data Base, which must be evaluated and corrected.

To insure the quality of the data used for the upper Arkansas River drainage basin geochemical maps, the data were thoroughly examined for errors, inconsistencies, and completeness. Each published NURE data release was compared with the corresponding records in the retrieved data. Several formatting problems were identified and corrected: correction of offset data columns, conversion of values to a common reporting unit (parts-per-million; ppm), comparing and compositing duplicate records into complete single records, and checking and correcting latitude-longitude coordinates. Additional records that were missing from the reformatted data were retrieved from original NURE tapes, reformatted, and added to the data base.

Each USGS data release report was also checked to insure the completeness and accuracy of retrieved data. When possible, the original laboratory paperwork was checked to confirm the sample media, to identify the methods of analysis and to verify the analytical data. Several records for stream-sediment samples that had received special treatment, such as heavy-mineral or magnetic-concentration techniques and partial leach analyses, were removed from the geochemical map data base. An early data base policy once allowed sample collectors to enter the latitude-longitude coordinates of the southwest corner of the 7½-minute map for all samples collected in that quadrangle; all records of samples with map-corner-point coordinates were also removed from the geochemical map data base. This data evaluation process consolidated and eliminated over 4,000 of the 14,000 records of data from the original retrieval.

Statistics and Combining of Data

After the data evaluation and correction procedure, the upper Arkansas River drainage basin data set consisted of 6,995 NURE records and 2,796 USGS records. The minimum value, maximum value, mean, and standard deviation for each of the three elements, analyzed by each method, are given in Table 2a.

Data that fall outside the normal analytical range are considered qualified data; these values are often qualified with a letter or symbol that denotes the element was not detected or detected at a value less than or greater than the accepted analytical range of the method and instrumentation. Table 2b lists the qualifiers and determination limits of each element by analytical method. To use qualified data in gridding and contouring algorithms, it was necessary to replace the qualified value with a real value. A value qualified with "N" was replaced with a real value equal to one-half the minimum unqualified value for that element. Values qualified with "L" were replaced with seven-tenths of the minimum unqualified value for that element, and "G" values were replaced by a real value equal to the maximum unqualified value for that element divided by seven-tenths. The actual replacement values used were based upon minimum and maximum values for the combined geochemical map data set and are listed in Table 2b.

Before combining the data from various analytical methods, the population distributions for each method were compared. Copper values in USGS data range from not detected at 5 ppm to 3,000 ppm Cu. In NURE data, the range is from the determination limit of 10 ppm to 4,339 ppm Cu with one outlier at 10,358 ppm Cu. A comparison of histograms showed that the distribution of concentrations from each set are very similar and a Student's *t*-test also showed that the two populations were similar at a 5% significance level; the significance level was improved when the outlier in the NURE data was removed from the data set.

Table 2a: Univariate statistics based on unqualified data by element and analytical method for the geochemical map data base.

Element- Method ¹	Min. Value	Max. Value	Mean Value	Standard Deviation	Valid Values	# of Qual. Values			
						B	L	N	G ²
USGS Samples									
Cu-OES	5	3000	43	88	2781	0	15	0	0
Pb-OES	10	20000	133	1109	2793	0	1	1	1
Zn-OES	200	10000	497	728	363	0	369	2062	2
Zn-AA	5	1500	99	106	1775	1015	NA	0	6
NURE Samples									
Cu-XRF	10	10358	50	197	6579	78	NA	338	NA
Pb-XRF	5	11481	67	393	6414	78	NA	503	NA
Zn-NAA	25	24760	241	761	5001	91	NA	1903	NA

Table 2b: Lower and upper determination limits by element and analytical method. A count of the qualified values reported at the indicated determination limit is given in parentheses.

Element- Method	Min. Value (Count)	L Value (Count)	N Value (Count)	G Value (Count)	New L ³ Value	New N Value	New G Value
USGS Samples							
Cu-OES	5 (57)	5 (15)	5 (0)	20000 (0)	3.5	2.5	28571
Pb-OES	10 (61)	10 (1)	10 (1)	20000 (1)	3.5	2.5	28571
Zn-OES	200 (154)	200 (369)	200 (2062)	10000 (2)	NA	NA	NA
Zn-AA	5 (3)	NA	5 (0)	1500 (6)	NA	2.5	35371
NURE Samples							
Cu-XRF	10 (48)	NA	10 (338)	NA	NA	2.5	NA
Pb-XRF	5 (132)	NA	5 (503)	NA	NA	2.5	NA
Zn-NAA	25 (2)	NA	** (1903)	NA	NA	2.5	NA

All values expressed as parts per million (ppm).

** Multiple values from 2 to 587 dependent upon sample composition.

¹ Analytical method: OES = DC-arc optical emission spectrography, AA = atomic absorption, XRF = X-ray fluorescence, NAA = neutron activation analysis.

² Qualified Values identified as follows: B = No value (not analyzed), L = Detected but less than the lower determination limit, N = Not detected, G = Greater than the upper determination limit, NA = Not applicable to this method.

³ A real value used to replace the corresponding qualified value. A value qualified with "N" was replaced with a real value equal to one-half the minimum unqualified value for that element. Values qualified with "L" were replaced with seven-tenths of the minimum unqualified value for that element, and "G" values were replaced by a real value equal to the maximum unqualified value for that element divided by seven-tenths. The actual replacement values used for each element were calculated from the minimum and maximum values for the combined geochemical map data set.

Lead values in USGS data range from not detected at 10 ppm up to greater than 20,000 ppm (>2% Pb); 10 samples have concentrations greater than 1.5% Pb. In NURE data, the range is from the determination limit of 5 ppm to 11,481 ppm Pb. A comparison of lead histograms shows that the distribution of concentrations from each set are similar although the USGS data appeared to be slightly biased towards higher values. A Student's *t*-test did not show that the two populations were similar at a 5% significance level until the 10 USGS outlier values greater than 1.5% Pb were removed from the USGS data set.

Zinc is often a difficult element to analyze using common multi-element analytical techniques. In the USGS data, zinc was primarily determined by a six-step, semi-quantitative DC-arc optical emission spectrography (OES) method (Grimes and Marranzino, 1968) with a lower determination limit of 200 ppm Zn. Because a large number of samples had concentrations of zinc below this determination limit, most projects had a selected subset of samples reanalyzed for zinc by an atomic absorption (AA) technique (O'Leary and Viets, 1986). In the NURE projects, zinc was analyzed by neutron activation analysis (NAA). Nunes and Weaver (1978) report the lower determination limit as 20 ppm Zn. In practice, the actual lower determination limit was variably higher or lower than the 20 ppm Zn and dependent upon the composition of the sample (see Planner and others, 1981). In the upper Arkansas River drainage basin, 28% of the samples in the NURE data set were below determination levels for zinc; these levels varied from 2 to 587 ppm Zn. Because of the large number of qualified values generated by each of the three analytical methods, comparisons between methods were difficult. A plot of AA-Zn versus OES-Zn for USGS samples analyzed by both techniques in the upper Arkansas River drainage basin showed unusually poor correlation between the two methods. On the basis of this comparison, the semi-quantitative nature of OES data and the 200 ppm Zn lower determination limit, a decision was made to eliminate all OES-Zn values from the USGS data set. A comparison of USGS AA and NURE NAA zinc histograms showed that the distribution of concentrations from the USGS data appear to be slightly lower than that of the NURE data. A Student's *t*-test did not show that the two populations were similar. These tests and comparisons were not entirely satisfactory for zinc because of the large number of qualified values.

A copper data base and a lead data base were created by combining records from both USGS and NURE studies. Despite the problems encountered with zinc, a zinc data base was created by combining the USGS AA zinc data with the NURE data set. Qualified values in each data base were then replaced with real values as given in Table 2b.

Data Gridding and Contouring Methods

The combined copper, lead, and zinc data bases were gridded and contoured with the EarthVision software package designed by Dynamic Graphics, Inc. A 1,000 by 1,000 meter grid was calculated from the scattered data for each element across the entire block of retrieved data. The large margin of data around the upper Arkansas River drainage basin study area insured that the interpretation of the data surface was continuous across the area and unaffected by any interpolation "edge effects" common to gridding and contouring algorithms. Each grid was graphically examined in conjunction with the actual data to verify the accuracy of the geochemical surface model with the data. Some isolated samples with high concentrations created undesirable spikes or anomalies in the grid. Further examination of these isolated samples revealed some biased stream-sediment samples that actually represented contamination from a single point source, usually a small mine site. These values were removed from the individual element data bases and the grids were recalculated so that the resulting geochemical maps would reflect regional trends rather than local effects. These high values included most of the outliers that caused problems in the statistical data set comparisons discussed above.

Contoured geochemical maps for each element were constructed from the gridded data (Appendix A). Contour intervals were chosen as multiples (1, 3, 5, 10, and 20) of elemental crustal abundance concentrations or Clarke Index values. Crustal abundance concentrations have been calculated by several researchers based upon averaged analyses from various combinations of crustal rocks (e.g., Parker, 1967; Fortescue, 1992). Although Shacklette and Boerngen (1984) calculated average amounts of 50 elements in soils and other materials, very little has been done to study average element abundances in stream sediments. The average

values chosen for copper, lead, and zinc (40 ppm, 20 ppm, and 75 ppm respectively) fall between Clarke Index values suggested by Fortescue (1992) and the values derived for western U.S. soils (Shacklette and Boerngen, 1984) and are based on empirical observations and regional stream-sediment geochemistry experience.

Data that plotted outside of the upper Arkansas River drainage basin study area were trimmed after the calculation of each grid and contour map to remove any interpolation and "edge effects" that might be present at the periphery of the data. The copper map was gridded from a data base containing 9,587 sites with valid copper data; 3,567 of the sites are within the boundary of the study area. The lead map was calculated from 9,712 sites with 3,602 sites internal to the area; the zinc map was calculated from 6,724 sites with 2,467 sites within the area. Small black dots show the location of each valid data point used to construct the geochemical maps in Appendix A.

Additional river-sediment samples were collected from the Arkansas River in 1993 and 1994 (Church and others, 1993; 1994) to determine the current dispersion of trace and heavy metals in river sediment from the Leadville area to the Pueblo Reservoir. Three additional geochemical dispersion maps of copper, lead, and zinc were created by adding a colored "ribbon" that represents the element concentration determined in that stretch of the Arkansas River (Appendix B). The river-sediment sample sites are plotted on the maps as small filled diamonds. Between sites, the "ribbon" was assigned a color based upon the element concentration determined at the downstream site. By overlaying these "ribbon" maps on the regional geochemistry maps, the effects of the geochemical composition of the geologic units and the extent of dispersed contamination from mining districts, smelter sites, industrial sources, and undisturbed mineralized areas can be estimated.

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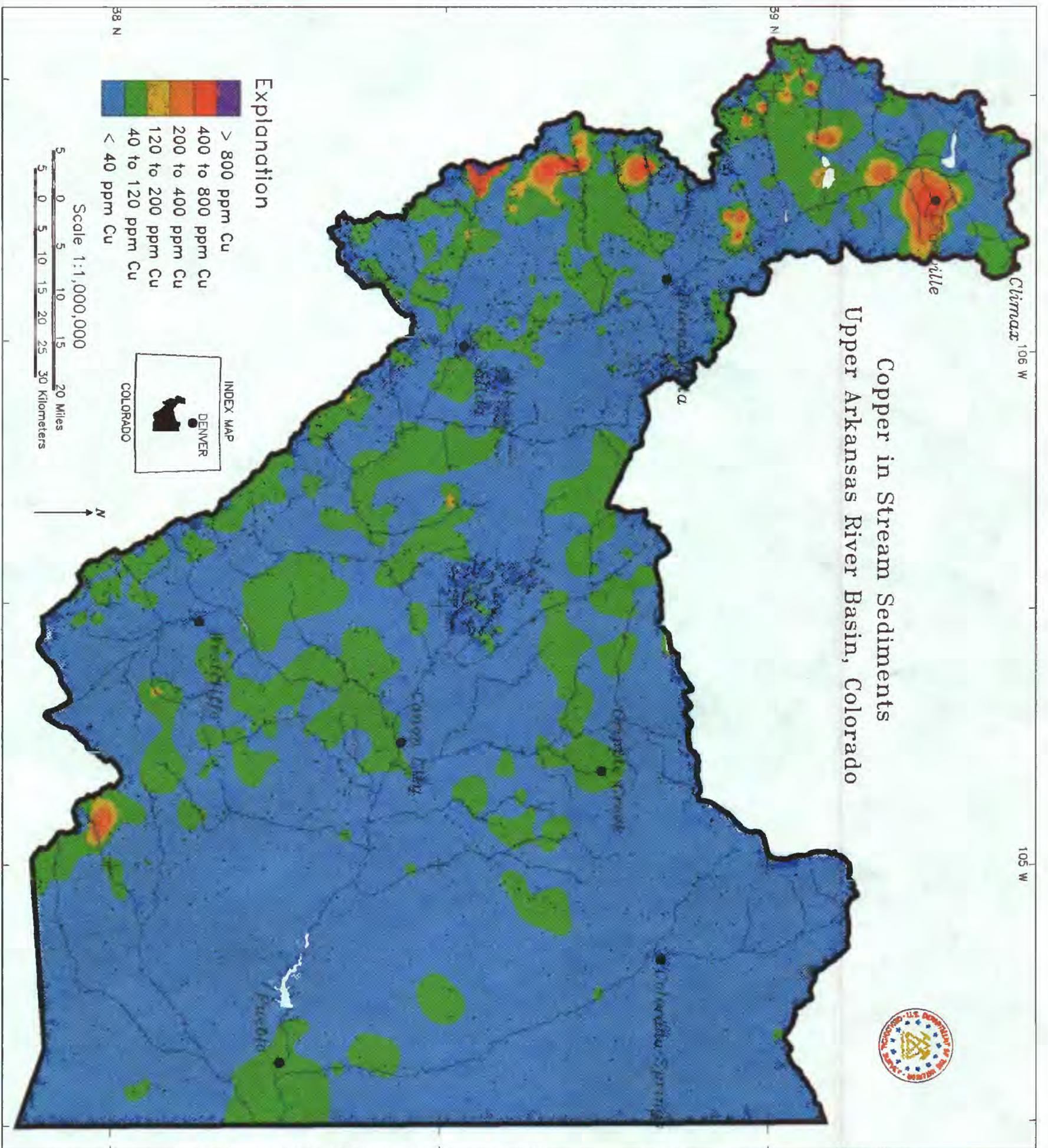
Appendix A: Geochemical maps showing the distribution of copper, lead, and zinc in stream sediments, the upper Arkansas River drainage basin, Colorado.

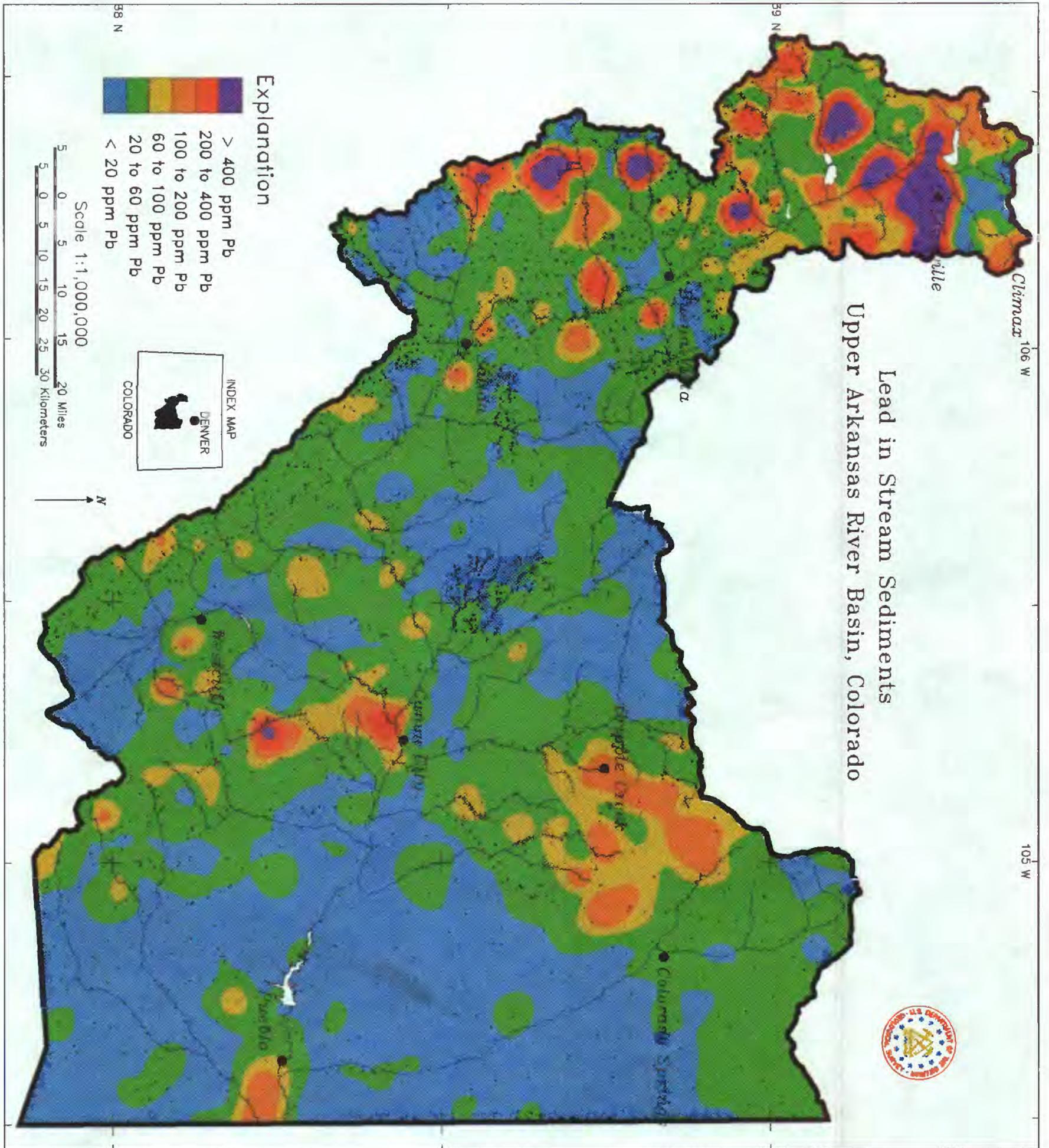
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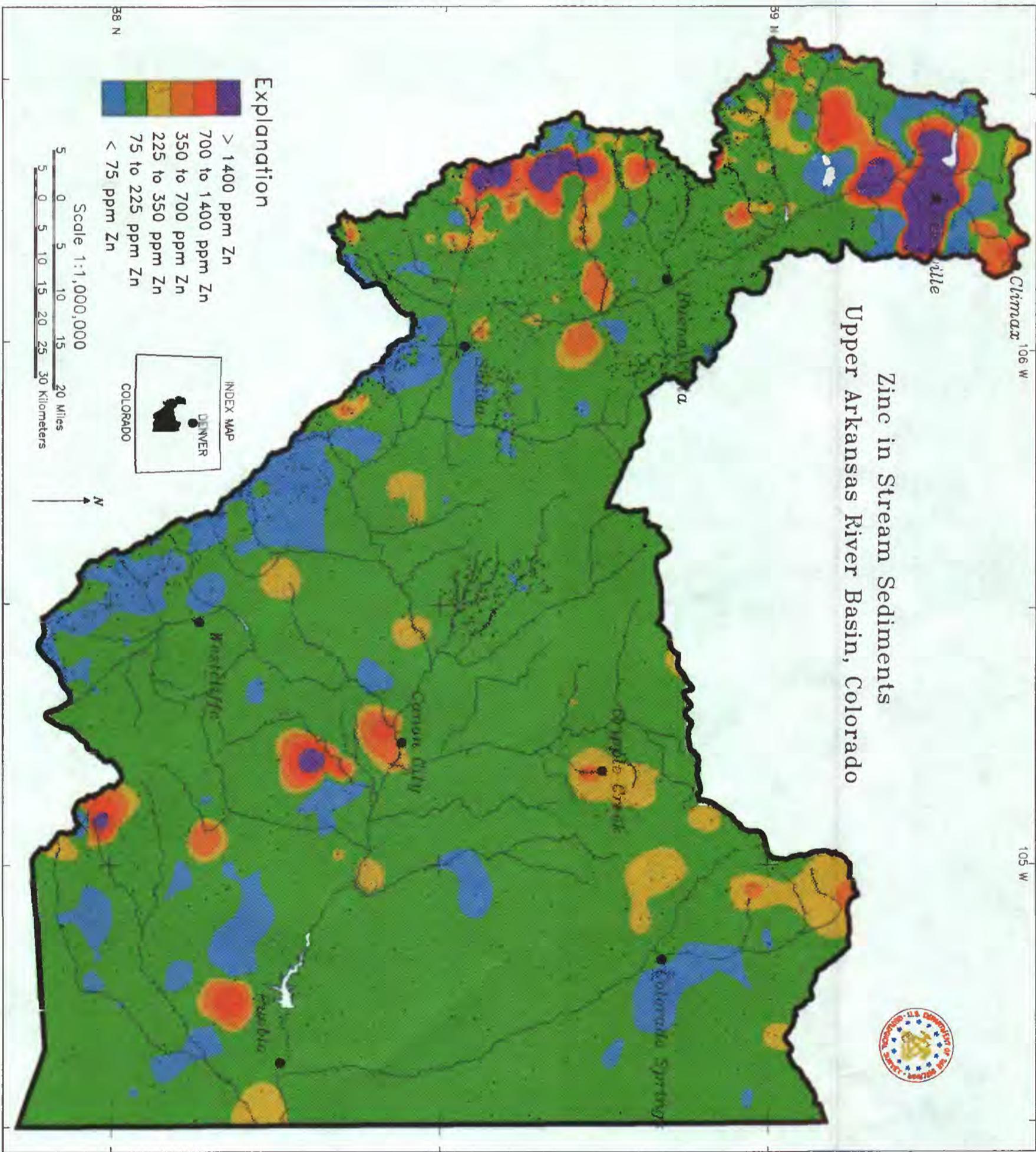
Copper in Stream Sediments, Upper Arkansas River Basin, Colorado

Lead in Stream Sediments, Upper Arkansas River Basin, Colorado

Zinc in Stream Sediments, Upper Arkansas River Basin, Colorado







Appendix B: Geochemical maps showing the dispersion of copper, lead, and zinc in river sediments down the upper Arkansas River, Colorado.

Contents

Copper Dispersion Down the Arkansas River, Upper Arkansas River Basin, Colorado

Lead Dispersion Down the Arkansas River, Upper Arkansas River Basin, Colorado

Zinc Dispersion Down the Arkansas River, Upper Arkansas River Basin, Colorado

