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Project Summary

Trace and Potentially Toxic Elements Associated with Uranium Deposits in South Texas

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The environmentally sensitive trace elements molybdenum, arsenic, and selenium are concentrated with uranium in ore deposits in South Texas. Cattle grazing in some pastures in mining areas have contracted molybdenosis, a cattle disease resulting from an imbalance of molybdenum and copper. To determine natural concentrations of the elements in soils in the South Texas area and to evaluate possible effects of mining on adjacent agricultural land, two sets of soil samples were collected and analyzed for molybdenum, arsenic, selenium, and copper. Two hundred and fifty-six samples were collected in a statistically random design from soils developed on the Whitsett Formation, Catahoula Formation, or Oakville Sandstone, the major uranium hosts of the area, and 182 samples were collected nonrandomly from areas of mining or mineralization to test specific hypotheses concerning the presence and origin of anomalously high concentrations of the elements.

Results of the random sampling show that the different geologic formations have different characteristic trace element concentrations. The Whitsett Formation has higher molybdenum (resulting from minor near-surface mineralization) and lower copper concentrations than the other two formations. With the exception of molybdenum in the Whitsett Formation and copper in all three formations, the trace element concentrations are similar to published average concentrations in soils worldwide.

Sampling in areas of mining and mineralization indicates that high concentrations of molybdenum, arsenic, or selenium occur dominantly in two situations: (1) in areas of shallow mineralization, resulting from natural processes, and (2) in drainages adjacent to older abandoned mines, resulting from runoff from the mines. Moderately high concentrations also occur in a few reclaimed areas. Windblown dust from mining areas has not measurably affected trace element concentrations in adjacent areas.

Comparison of molybdenum and copper concentrations in soils and grasses and theoretical considerations of the availability to plants of molybdenum and copper in soils suggest that forage in much of the area studied could have anomalously low copper/molybdenum ratios — low enough to induce molybdenosis in cattle.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Open-pit mining in South Texas began in the late 1950s and, in 1954, uranium deposits were discovered in the area. Mining and uranium production have increased steadily and Texas is currently ranked the nation's third leading producer of uranium (behind Wyoming and New Mexico), solely on the basis of mining in South Texas.

Several environmentally sensitive trace elements (molybdenum, arsenic, and selenium) are known to be associated with the South Texas uranium deposits. Mining brings to the surface material previously buried, thus introducing the potential for contamination of neighboring agricultural areas and water supplies. Since some uranium mineralization also occurs near the surface, high concentrations of the trace elements could occur naturally in soils in mineralized areas.

The purpose of this study is (1) to establish baseline concentrations of the potentially toxic elements throughout most of the uranium mining area, (2) to determine whether significantly high concentrations exist and, if so, in what settings they exist, and (3) to evaluate several potential mechanisms of pollution; e.g., the transport of high concentrations of trace elements away from a mining site and the resultant contamination of adjacent areas. Systematically collected samples of soil and grass were analyzed for the elements molybdenum, arsenic, selenium, and copper.

Physical Setting

To interpret the origin, distribution, and environmental significance of trace elements in soils, it is necessary to understand (1) the geologic substrate—the parent material of soils; (2) the soils themselves — their nature, origin, and derivation from geologic substrates in a particular climatic setting; and (3) the geochemistry of the elements—how and why they occur in various concentrations in substrates and soils.

Geology

Within the South Texas area, three geologic formations (Fig. 1) are of immediate interest: (1) the Whitsett Formation of the Jackson Group, (2) the Catahoula Formation, and (3) the Oakville Sandstone. Almost all of the present uranium mining and identified uranium mineralization occurs in these three formations.

The Whitsett Formation of the Jackson Group consists of interbedded sands and muds deposited in a strandplain-barrier bar system. The sands are dominantly strike oriented, were deposited in a strandplain environment, and are major hosts of uranium ore deposits. Lagoonal or shelf muds were deposited between the sands. Major dip-oriented, channel sands occur irregularly along the line of outcrop and are also mineralized.

The Catahoula Formation in the study area (Karnes and Live Oak Counties) consists of interbedded sands and tuffaceous muds deposited in a fluvial environment. Throughout most of Live Oak and Karnes Counties, the Catahoula outcrop consists of interchannel muds deposited between major channels to the northeast and the southwest.

The Oakville Sandstone was also deposited by a major fluvial system, but in the Karnes-Live Oak area the Oakville has a much higher sand content than the Catahoula Formation. The Oakville Sandstone was fed by four major river systems, two of which occur in the Karnes-Live Oak area. Thus, outcrops of the Oakville are mostly sand-rich; a few muddier areas occur in interchannel deposits.

Soils

The compositions of soils in the study area are strongly influenced by the compositions of the substrates. However, individual soils are not restricted to individual formations because similar substrates commonly occur in different formations. In general, four broad, distinct but overlapping groups of soils correlate with the distinct substrate types. The largest group consists of alkaline, calcareous clay-rich soils developed on muddy parts of the Whitsett Formation, on the mud substrates of the Catahoula Formation, and on the rare, high-mud parts of the Oakville Sandstone. The clay soils are relatively fertile and commonly heavily farmed. Another group consists of sandy to rocky soils developed on or adjacent to sands and indurated sands of the Whitsett Formation. Soils developed on the nonindurated sands of the Oakville Sandstone are of intermediate to sandy texture. Bottomland soils developed on Quaternary alluvium constitute a fourth group.

Geochemistry of Molybdenum, Arsenic, Selenium, and Copper

Molybdenum, arsenic, and selenium are geochemically associated with uranium and are concentrated in uranium ore deposits. The elements are soluble in oxidizing, neutral to alkaline water as anions ($MoO_4^{=}$, AsO_4^{3-}, $SeO_3^{=}$, or $SeO_4^{=}$). With decreasing Eh, the trace elements are precipitated in a lower valence state commonly as sulfides, as minor constituents of pyrite, or as the native element.

Unlike molybdenum, arsenic, selenium, or uranium, copper is soluble in acidic water and insoluble in the moderate or high pH waters in which the other elements are soluble. Copper thus is not concentrated with uranium or molybdenum.

Trace elements exist in various forms in soil, and not all are equally available to plants. Major factors that govern availability of molybdenum, arsenic, and selenium are pH and drainage status, although organic content, sulfate content, and other factors may also be significant. At high pH, a large proportion of the elements are desorbed, in solution, and available to plants. Copper availability is also affected by pH and drainage status. However, unlike the other elements, copper is more available at low pH and uptake by plants is severely limited at pH of 6 or above. In the predominately alkaline soils of the South Texas uranium mining areas, molybdenum, arsenic, and selenium should be relatively more available to plants than copper.

Soil Sampling

The soil samples collected fall into two general categories: background samples, designed to determine the natural range and scale of variation of concentrations in soils of the uranium mining region, and samples from mining and mineralized areas. Background sampling is random. Mining and mineralization area sampling is nonrandom and includes sampling areas of shallow mineralization and of mining where anomalous concentrations could be encountered.

Random-sampling background concentrations were obtained for two purposes: to determine the natural geochemical environment and to provide a baseline with which to compare concentrations in soils in mining and mineralized areas. Both purposes require random sampling designs so that the samples collected are representative of the sampled area and show the normal range of concentrations of an element. Also, the design should allow statistical treatment of the data. The sampling design used here is generally called stratified random sampling with natural strata.

Random Sampling

Sampling was divided into a number of levels; the highest level is the South Texas uranium mining region. Within this region, The Whitsett Formation, Catahoula Formation, and Oakville Sandstone form the first sublevels (Fig. 1). To

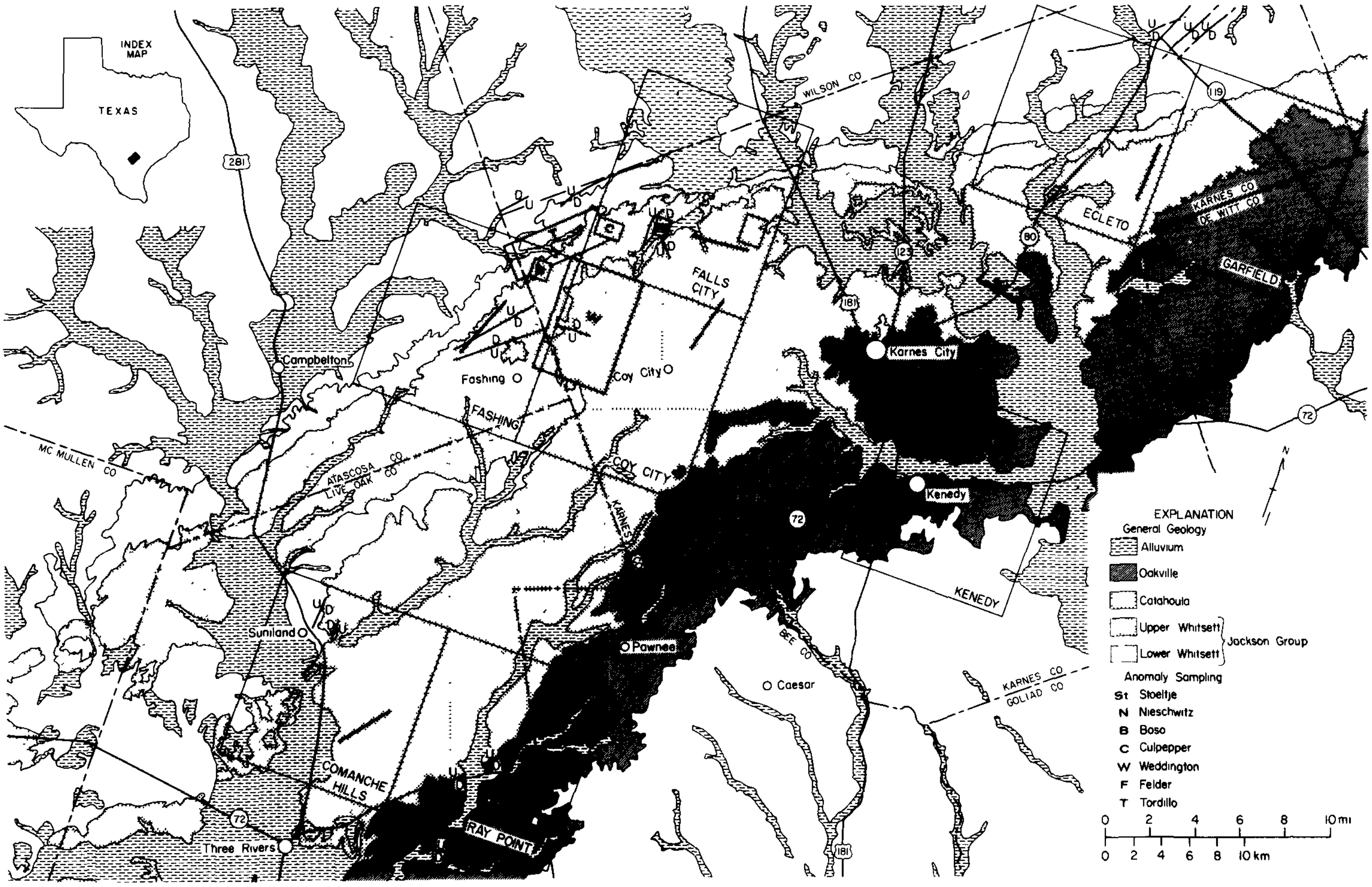

Figure 1. *Index map of a part of the South Texas uranium mining district, showing geology and location of background sampling and mining and mineralized area sampling. Large outlined areas are quadrangles of background sampling. Heavy line within each quadrangle is approximate location of sampling barbell.*

test geographic variation within each formation, the uranium mining region was divided into three geographic units: southwestern, central, and northeastern. Within each unit a 7.5-minute quadrangle (Fig. 1) was selected to be the second sublevel of sampling. The quadrangles were limited in that one of the formations had to occur within the quadrangle.

Variations in trace element concentrations at different scales were determined within each quadrangle by a barbell sampling design (Fig. 2). Each barbell is constructed by randomly selecting a point and a direction (derived from random number tables). The point is used as the midpoint of a line 4.096 km long that trends in the selected direction. The end points of this line define the midpoints of two new lines with randomly selected directions. This process is repeated three times with lines 512 m, 64 m, and 8 m long. The end points of the 8 m lines are sampling locations.

At each location, samples were collected from the A and B soil horizons. Thus there are a total of 16 locations and 32 soil samples from each quadrangle. Standard statistical analysis, including analysis of variance, was used on all results.

Sampling in Areas of Mining and Mineralization

Samples in areas of mining or shallow mineralization were collected non-randomly from specific locations to test hypothesized processes or concepts. Thus samples were collected upwind (southeast) and downwind (northwest) of mining areas to determine if wind transport of exposed ore or overburden could affect molybdenum or other trace element concentrations in soils adjacent to the mining area. In areas of suspected or identified shallow mineralization, sample traverses were made across the mineralized zone. Where erosion of spoil piles had broken down former protective berms, samples were taken of the eroded material and in drainages downstream.

Results of Random Sampling

Table 1 summarizes basic statistics of the analyses from the random sampling program; the results are tabulated by formation and quadrangle.

Statistical Interpretation

Analysis of variance shows that within each quadrangle of all three formations a major part of the variance is at the lowest level, between the A and B horizon samples. The percentage of variance in

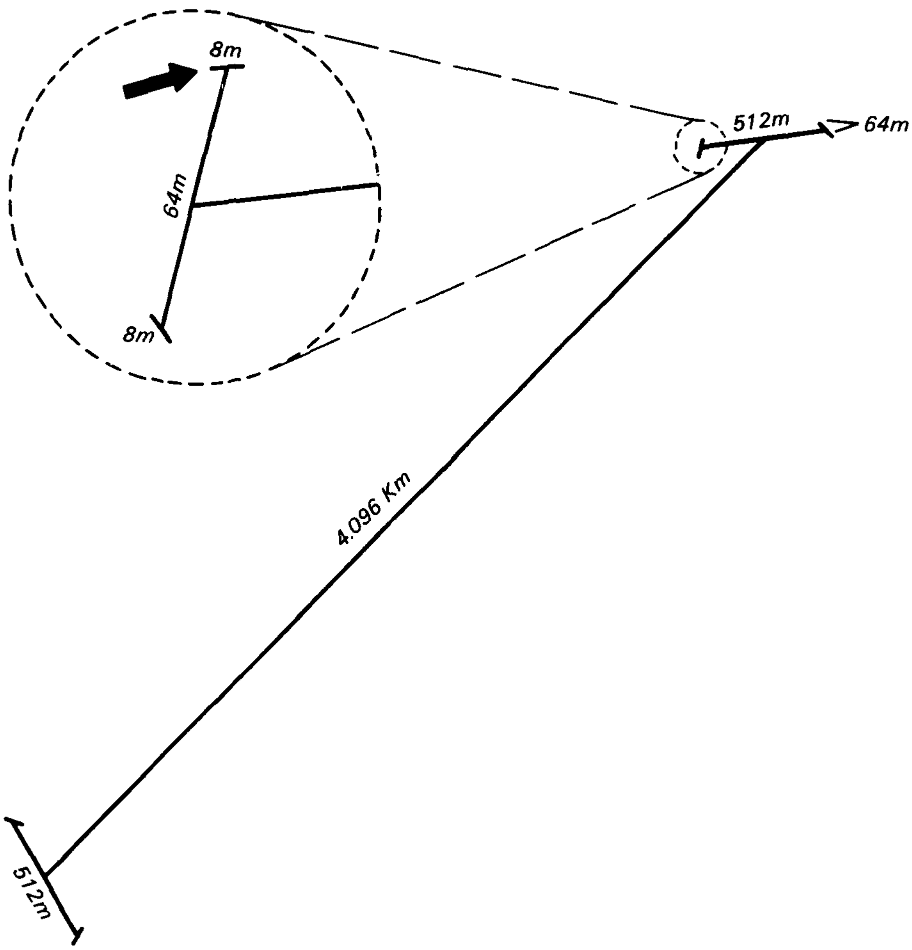

Figure 2. General configuration of the barbell sampling scheme.

molybdenum concentrations at the lowest level ranges from 19 percent (Catahoula-Ecleto) to 70 percent (Catahoula-Comanche Hills). Very little of the variance occurs at the highest level, between sample groups 4.096 km apart. Only the Oakville (Ray Point) samples have very much of the variance, 38 percent, at the highest level. For all other quadrangles, variance at this level comprises no more than 3 percent of the total.

Most variance that is not at the lowest level is at intermediate distance levels, and mostly at 512 m or 64 m. For example, all the variance in the Whitsett (Fashing) samples is at the lowest level (44 percent) or the 512-m level (56 percent). Variance at the 512-m level is significant at the 0.01 probability level. Other quadrangles have roughly similar patterns.

In general, similar patterns exist for selenium, copper and arsenic results. Most variance is at the lowest level, much of the rest is at an intermediate distance level, and variance at the highest level is very low with only a few exceptions.

To establish a geochemical baseline, an "expected range" was designated as the central 95-percent range of concentrations assuming lognormal distribution. Only one concentration in 20 should fall outside the central 95-percent range and only one in 40 should lie above the range. Because this study is concerned primarily with anomalously high concentrations, we have provided only the upper limit of the expected range (Table 1). Because almost all variance occurs at scales less than 4.096 km, the upper limit for a quadrangle should be applicable throughout the area of the quadrangle.

Correlation with Geology

Several conclusions result from relating the analytical results to geology. First, the different geologic formations have different trace element concentrations. This pattern is most obvious for molybdenum. The Whitsett (Fashing) samples contain the highest molybdenum concentrations and have the highest variance — they have the greatest range of molybdenum concentrations of the various formations. Because the Whitsett Formation was sampled only in the Fashing Quadrangle, which includes areas of shallow mineralization and anomalous radioactivity, characterization beyond the boundaries of the quadrangle is unwarranted. The high concentrations probably result from the derivation of the soils from mineralized rock.

The Catahoula Formation and Oakville Sandstone have lower concentrations and are geographically uniform; there is not a regional pattern to the concentrations. The Oakville Sandstone is particularly homogeneous with very similar means (0.82-0.91 ppm) and ranges from each quadrangle. The Catahoula Formation is also relatively homogeneous, but the Catahoula (Ecleto) samples (the northeasternmost quadrangle sampled) have slightly higher means and higher variance than other Catahoula samples, reflecting a few distinctly higher molybdenum concentrations.

Selenium shows a similar, but less pronounced, pattern to molybdenum. Arsenic was analyzed for only two quadrangles, and too little data exist to make any major conclusions. Nevertheless, Whitsett (Fashing) samples have greater arsenic concentrations than Catahoula (Coy City) samples. This relationship generally agrees with the molybdenum and selenium patterns. Copper, analyzed for five quadrangles, shows the reverse pattern. Whitsett samples have the lowest copper concentrations.

Comparison with Concentrations in Other Soils

From comparison with published summaries of trace element concentrations in soils, it can be concluded that most soils in the uranium mining areas have molybdenum, arsenic, and selenium concentrations similar to other natural soils around the United States, and worldwide. However, some soils developed on the Whitsett Formation have measurably higher molybdenum concentrations, and all soils have distinctively lower copper concentrations, compared to natural soils from a variety of locations.

Table 1. *Summary of Basic Statistics (all concentrations in ppm)*

Formation	Quadrangle	Range	Means Arithmetic	Means Geometric	Variance	Standard Deviation	Upper Limit for Expected Range	No. of Outlier
				Molybdenum				
Whitsett	Fashing	0.2 - 4.6	2.1	1.8	0.86	0.93	6.05	0
Catahoula	Ecleto	0.3 - 4.0	1.1	0.95	0.56	0.75	3.19	1
	Falls City	0.2 - 1.0	0.69	0.66	0.039	0.20	1.33	0
	Coy City	0.5 - 1.6	0.99	0.97	0.046	0.22	1.60	1
	Comanche Hills	0.4 - 1.4	0.73	0.71	0.026	0.16	1.10	1
Oakville	Garfield	0.4 - 1.3	0.84	0.80	0.066	0.26	1.53	0
	Kenedy	0.5 - 1.2	0.82	0.80	0.043	0.21	1.34	0
	Ray Point	0.3 - 2.0	0.91	0.84	0.146	0.38	1.89	1
				Selenium				
Whitsett	Fashing	0.01 - 0.90	0.18	0.10	0.038	0.20	1.10	0
Catahoula	Ecleto	0.03 - 0.60	0.15	0.117	0.019	0.14	0.47	2
	Falls City	0.01 - 0.30	0.18	0.16	0.005	0.07	0.53	0
	Coy City	0.01 - 0.31	0.07	0.04	0.004	0.07	0.32	0
	Comanche Hills	0.02 - 0.26	0.13	0.117	0.0026	0.05	0.32	0
Oakville	Garfield	0.10 - 0.30	0.19	0.19	0.003	0.05	0.32	0
	Kenedy	0.01 - 0.38	0.14	0.09	0.010	0.10	0.87	0
	Ray Point	0.09 - 0.37	0.19	0.18	0.003	0.05	0.32	1
				Copper				
Whitsett	Fashing	3.4 - 8.3	5.5	5.4	1.6	1.3	8.39	0
Catahoula	Ecleto	2.9 - 20	8.0	7.9	9.2	3.0	14.0	1
	Coy City	4.2 - 12	8.6	8.4	4.0	2.0	13.8	0
	Comanche Hills	6.1 - 13	10.8	10.7	2.1	1.4	14.0	0
Oakville	Ray Point	7.9 - 13	10.1	10.0	2.0	1.4	13.1	0
				Arsenic				
Whitsett	Fashing	0.6 - 17	5.3	4.6	8.2	2.9	13.8	1
Catahoula	Coy City	0.2 - 6.9	3.4	2.7	3.2	1.8	12.7	0

Results of Mining and Mineralized Area Studies

The locations of seven areas of mining or mineralization sampled for this study are shown in Figure 1. To identify anomalously high concentrations, these samples are compared to the expected ranges determined from the random sampling. The particular range used is determined by the formation and quadrangle in which the tested sample lies.

Anomalously high concentrations of molybdenum, arsenic, and selenium exist in three settings: (A) in areas of shallow mineralization, (B) in drainages adjacent to older, abandoned mines, and (C) in some reclaimed areas. High concentrations have not apparently resulted from wind transport.

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***S. Jackson Hubbard** is the EPA Project Officer (see below).*
The complete report, entitled "Trace and Potentially Toxic Elements Associated with Uranium Deposits in South Texas," (Order No. PB 83-154 054; Cost: $13.00, subject to change) will be available only from:
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