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Applications of Trace-Element and Stable-Isotope Geochemistry to Wildlife Issues, Yellowstone National Park and Vicinity

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Integrated Geoscience Studies in the Greater Yellowstone Area—Volcanic, Tectonic, and Hydrothermal Processes in the Yellowstone Geoecosystem

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Abstract

Reconnaissance investigations have been conducted to identify how geochemical techniques can be applied to biological studies to assist wildlife management in and near Yellowstone National Park (the Park). Many elements (for example, As, B, Be, Ce, Cl, Cs, F, Hg, K, Li, Mo, Rb, S, Sb, Si, and W) are commonly enriched in (1) thermal waters in the Yellowstone area, (2) rocks altered by these waters, (3) sinter and travertine deposits, and (4) soils and stream sediments derived from these rocks. Some of these elements, such as As, F, Hg, and Mo, may be toxic to wildlife and could be passed up the food chain to many species of animals.

Three investigations are described here. The first discusses the abundance and distribution of selected elements in the scat (feces) of bison *(Bison bison*), elk (*Cervus elaphus*), and moose (*Alces alces*) collected in and near the Park from areas underlain by both unaltered and hydrothermally altered rock. As compared to mean values for stream-sediment analyses, those of scat analyses collected in the Yellowstone area show relatively high concentrations for 12 elements. This suite of elements comprises (1) hydrothermally related elements (As, Br, Cs, Mo, Sb, and W), (2) essential major elements for plants (Ca and K) and some trace elements (Ba, Rb, and Sr) that commonly proxy (substitute) for Ca or K, and (3) zinc. The behavior of zinc is not understood. It is an essential element for plants and animals but does not normally proxy for either Ca or K. Zinc is also not related to hydrothermal activity. This unique behavior of zinc is discussed in other parts of this investigation.

Six elements (Cr, Hg, Ni, Pb, Se, and U) that can be toxic to wildlife are present in low concentrations in scat, reflecting their generally low concentrations in rock and stream-sediment samples collected throughout the Park.

The chemistry of large-animal scat provides information on the feeding habits of large animals in the Park. Scat chemistry shows a high spatial correlation with fossil or active thermal areas or with areas immediately downstream from thermal areas. The longer that animals forage in these localities, the more likely it is that they may ingest significant amounts of potentially toxic elements such as arsenic.

A second investigation describes the concentration levels of hydrothermal mercury and other elements in cutthroat trout (*Oncorhynchus clarki bouvieri*) and lake trout (*Salvelinus namaycush*). These elements are derived from sublacustrine hot springs and their habitats in Yellowstone Lake, and this study demonstrates that mercury can be used as a tracer in animal ecology studies. Mercury concentrations are significant in the muscle (average 0.9 ppm, dry weight for both) and liver (average cutthroat = 1.6 ppm, dry weight; average lake trout = 2.1 ppm) of cutthroat and lake trout populations. The mercury levels in fish are believed to be related to mercury introduced to the lake by sublacustrine hot springs, which have dissolved mercury concentrations of as much as 0.170 ppb. Methylation of mercury in thermal waters is probably carried out by methanogenic or sulfate-reducing bacteria that live around sublacustrine hot springs and are consumed by crustaceans such as amphipods, which are a major food source for the cutthroat trout. The mercury levels in the cutthroat trout are transferred to lake trout and to land animals that eat trout. For example, hair of grizzly bears that have been collected near Yellowstone Lake have high mercury levels (0.6–1.7 ppm, dry weight), whereas hair of bears sampled at more remote areas in the greater Yellowstone ecosystem have low mercury contents (0.006–0.09 ppm, dry weight). This observation provides strong evidence that mercury in grizzly bears is derived from feeding on spawning cutthroat trout in the spring and early summer. Studies of mercury and metal contents in other grizzly bear food sources (plants and animals) show that only cutthroat trout are strongly enriched in mercury. These data can potentially be used to quantify the percentage of the bear population that eats cutthroat trout and to determine how far individual bears travel to Yellowstone Lake to eat them.

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A third investigation describes carbon-, nitrogen-, and sulfur-isotope compositions in grizzly bears and in some of their foods and describes how these data can be applied to studies of grizzly bear demographics. $\delta^{13}C$ values in the Yellowstone ecosystem range from –21.7 ‰ to –30.4 ‰, a range that reflects the influence of C_3 plants on the carbon reservoir and probably the effect of elevation on physiological processes. $\delta^{15}N$ values range from –2.3 ‰ to 11.0 ‰ and show classical trophic enrichments with respect to most grizzly bear food sources. Cutthroat trout $\delta^{15}N$ values (8.3±1.0 ‰) may reflect the importance of sublacustrine hydrothermal springs to the food chain in Yellowstone Lake. Lake trout have even larger $\delta^{15}N$ values (11.0±0.4 ‰) that are consistent with their feeding on cutthroat trout. Grizzly bear $\delta^{15}N$ values range from 7.0 ‰ to 8.8 ‰. Although grizzly bears are known to eat cutthroat trout, trophic enrichment in $\delta^{15}N$ above values found in trout is not apparent in analyses of bear hair. This discrepancy occurs because $\delta^{15}N$ values are averaged over one year and include the significantly lower $\delta^{15}N$ values of vegetable food sources consumed by bears while their hair is growing. $\delta^{34}S$ values in the ecosystem range from –3.1 ‰ to 11.1 ‰. $\delta^{34}S$ values of fish (1.2±0.5 ‰) are nearly the same as those in sulfate from thermal springs. Vegetation (clover, cow parsnip, and spring beauty), ungulates (deer, elk, and bison), and moths show a greater range of $\delta^{34}S$ values (–3.3 ‰ to 3.2 ‰). However, bears show higher $\delta^{34}S$ values (3.2 ‰ to 5.4 ‰ in muscle and 6.1 ‰ to 8.7 ‰ in hair) that are consistent with the consumption of whitebark pine nuts ($\delta^{34}S$ = 8.3 ‰ to 11.4 ‰). $\delta^{34}S$ values in bears and their food sources seem to be constrained by the major sources of sulfate and sulfide sulfur in the igneous and sedimentary rocks that underlie much of the Park. The large $\delta^{34}S$ values found in bear tissues are consistent with the documented fact that most grizzly bears eat substantial amounts of whitebark pine nuts when available. This consumption occurs during hair growth in the fall, thus providing an isotopic marker that may be useful in quantifying nut consumption in individual bears.

These three studies show some different ways that geochemical techniques can be applied to biologic issues. The results suggest that integration of geochemistry into specific biologic studies may help address issues of interest to wildlife managers in Yellowstone National Park and the greater Yellowstone ecosystem.

Introduction

Yellowstone National Park (the Park) is known worldwide for spectacular scenic beauty, awesome hydrothermal features, and varied wildlife. These are intertwined and closely associated with the geology and geochemistry of the Park. We describe below how trace-element and stable-isotope geochemical techniques can be applied to wildlife issues in Yellowstone National Park. The greater Yellowstone ecosystem is an excellent natural laboratory in which to examine the relationship between geochemistry and wildlife because of (1) the large knowledge base acquired by geoscientists from many years of investigating the chemistry of rocks and thermal waters and (2) the unique chemical and isotopic signatures that result from hydrothermal activity. The trace-element and isotopic compositions of the unaltered Tertiary and Quaternary volcanic rocks that compose the bedrock in the Park are well known or easily inferred. Hydrothermal fluids, which are characterized by enrichments in elements such as As, B, Be, Ce, Cl, Cs, F, Hg, K, Li, Mo, Rb, S, Sb, Si, and W, leave a well-understood trace-element and stable-isotope imprint on hot-spring deposits and altered rocks. These differences between the trace-element content and stable-isotope compositions of altered rocks and hot-spring deposits and those in unaltered rocks can be used as indicators of animal diet, ecology, and demographics. Many of the trace elements that are enriched in thermal waters are potentially toxic to wildlife. However, few studies of such toxicity have been conducted.

In cooperation with the National Park Service, the U.S. Geological Survey investigated three aspects of the relationship between environmental and isotopic geochemistry and the wildlife of Yellowstone National Park. In the first study, samples of bison (*Bison bison*), elk (*Cervus elaphus*), and moose (*Alces alces*) scat were collected from areas in and near the Park, including areas of hydrothermally altered rocks in active geyser basins, areas of rocks altered by fossil hydrothermal activity, and areas of unaltered rocks. When large animals forage in areas of hydrothermally altered rock, they eat plant material, which commonly includes some attached inorganic substrate. Both the plant material and the inorganic matter may contain high concentrations of potentially toxic elements. Those animals that forage mostly in hydrothermally affected areas thus have a greater risk for trace-element poisoning.

Previous investigations (Garrott and others, 2002) showed that the health of elk living in some areas in the Park was significantly impacted by high hydrothermal fluorine concentrations in their diet. Except for fluorine, we know very little about the effects of hydrothermal elements on large Park animals. Although we can demonstrate that animals are ingesting potentially toxic elements, we do not know how much of a given element is accumulated in the animals and what levels may impact their health.

A second study evaluated the concentrations of selected elements in trout collected from Yellowstone Lake. The native cutthroat trout (*Oncorhynchus clarki bouvieri*), a threatened species, is particularly important to the lake ecosystem because they spawn in the tributaries to the lake and are important food sources for otters, bears, and eagles. The presence of exotic, predatory lake trout (*Salvelinus namaycush*) in Yellowstone Lake severely threatens the viability of the native cutthroat. Cutthroat trout have been observed to congregate and feed around shallow-water hydrothermal vents in Yellowstone Lake and, therefore, accumulation of trace metals in the fish was investigated. Further, transference of potentially toxic trace elements, especially mercury, from cutthroat trout into the food chain was evaluated in conjunction with stable-isotope studies of grizzly bear food sources.

In the third study, stable isotopes were measured in the hair and flesh of grizzly bears (*Ursus arctos*) and in several

common bear foods. The grizzly bear is listed as a threatened species in the conterminous United States. In the greater Yellowstone ecosystem, grizzly bears rely on an array of plant and animal foods, but the majority of the diet comprises four major items: ungulates, cutthroat trout, army cutworm moths, and vegetation, especially whitebark pine nuts. Historically, biologists have used scat analysis to determine bear diets, but differential rates of digestion make quantitative assessments of intake difficult. We explored the possibility of using stable-isotope signatures in the hair and tissue of the grizzly to help quantify food consumption and eating habits. Stable-isotope studies of grizzly bear tissue (hair from living bears and muscle tissue from carcasses) and the most important foods in bear diets show a large range in $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ values. These variations reflect geologic and environmental sources in the greater Yellowstone ecosystem and well as trophic enrichments in the food chain.

These three investigations demonstrate how geochemical techniques widely used in the earth sciences can be applied to biological studies to assist wildlife management in Yellowstone National Park as well as in the greater Yellowstone ecosystem.

Associations Between the Chemistry of Rock, Stream Sediment, and the Scat of Bison (*Bison bison*), Elk (*Cervus elaphus*), and Moose (*Alces alces*)

In Yellowstone National Park, the chemistry of thermal waters and their associated deposits is largely controlled by that of the underlying bedrock. Most of the fossil and active thermal areas are in or near exposures of Quaternary rhyolitic volcanic rocks. In these areas, as discussed in Rye and Truesdell (1993; this volume), meteoric waters percolate to various depths; become heated as they approach hotter rocks at depth; accumulate magmatic gases such as He, CO_2, and H_2S; and rise to the surface through an elaborate plumbing system in geyser and hot-spring basins. As they migrate to the surface, these waters leach elements from the rock units through which they pass. They also mix with local ground waters, which results in a diversity of hydrothermal-water compositions that may vary significantly, even on a local scale.

Recent Park-wide studies (Miller and others, 1997) have shown that a generally common suite of elements, including As, B, Be, Ce, Cl, Cs, F, K, Li, Mo, Rb, S, Sb, Si, and W, is brought to the surface by thermal waters. Many of these elements are deposited in hydrothermally altered rocks. Our study of the chemistry of fresh and hydrothermally altered rocks and related travertine and sinter deposits, as well as stream sediments eroded from these source areas and carried downstream through, and out of, the Park (Chaffee and others, this volume), indicates that altered volcanic rocks are commonly enriched in as many as 11 elements (As, Au, Br, Cs, F, Hg, Mo, S, Sb, Se, and W). Similarly, Sturchio and others (1986), in a study of hydrothermal alteration in drill core from Yellowstone thermal areas, found strong enrichment of Cs, Li, and Sb. Arsenic, F, Hg, Mo, and possibly Sb are of particular interest because they are potentially toxic to wildlife.

Siliceous-sinter deposits in major geyser and hot-spring basins, such as the Upper, Midway, Lower, Shoshone, and Norris Basins, as well as sediments derived from these deposits, are enriched in many of these same 11 elements listed above (Thompson and DeMonge, 1996; Fournier and others, 1994). Less abundant travertine deposits in hot-spring areas such as Mammoth are underlain by carbonate bedrock (mainly the Mississippian Madison Group). Thermal waters from these areas tend to be enriched in calcium (Thompson and DeMonge, 1996; Fournier and others, 1994) but also contain many of the 11 elements listed above.

Plant species growing in hydrothermally altered areas take up varying amounts of the hydrothermally derived elements, some of which are essential for growth. As an example, analyses of some plant species growing in, or downstream from, altered areas in the Park yield tens of parts per million arsenic (dry weight basis) (James Otton, oral commun., 2000). Some hydrothermally derived elements may also be present as wind-borne surface coatings or rain-splatter deposits on plant parts. By inference, other hydrothermal elements could be present in elevated concentrations in plants growing in hydrothermally affected areas.

Some of the elements discussed here (for example, As, F, Hg, and Mo) can adversely affect the health of wildlife (Gough and others, 1979; Shupe and others, 1984). Although these elements have long been known to be present in surface waters in and near the hydrothermally altered areas of the Park (see, for example, Ball and others, 1998; Miller and others, 1997; Stauffer and others, 1980), it was not known whether large animals such as bison (*Bison bison*), elk (*Cervus elaphus*), and moose (*Alces alces*) actually ingest significant quantities of these elements in their food. To better understand the chemistry of material ingested and excreted by bison and elk, and to a lesser extent by moose, we analyzed samples of their scat (feces) collected from areas of unaltered (mainly volcanic) rocks located throughout the Park and vicinity and from areas of hydrothermally altered rocks, which crop out mainly in geyser basins. These data were then compared to similar data for rock and stream sediment collected from throughout the Park and vicinity.

Only two articles in the literature (Day and others, 1985; Robinson, 1986) were found to contain analytical data for scat. These data, however, were presented in the context of exploration for mineral deposits in Alaska and Arizona, respectively. Thus, no chemical baseline existed for animal scat in Yellowstone National Park prior to this study. The scat chemical data determined for this investigation were evaluated to determine (1) the abundances and distributions of elements and (2) the common associations of elements. The spatial variations of selected elements were examined to investigate whether there are spatial relationships between (1) anomalous elements in scat samples and (2) geyser basins and other thermal features. The results of these studies identify some hydrothermally associated, potentially toxic elements that have been consumed by large animals and suggest how far these animals may have traveled from the time they consumed the plants in an altered area until they deposited their scat.

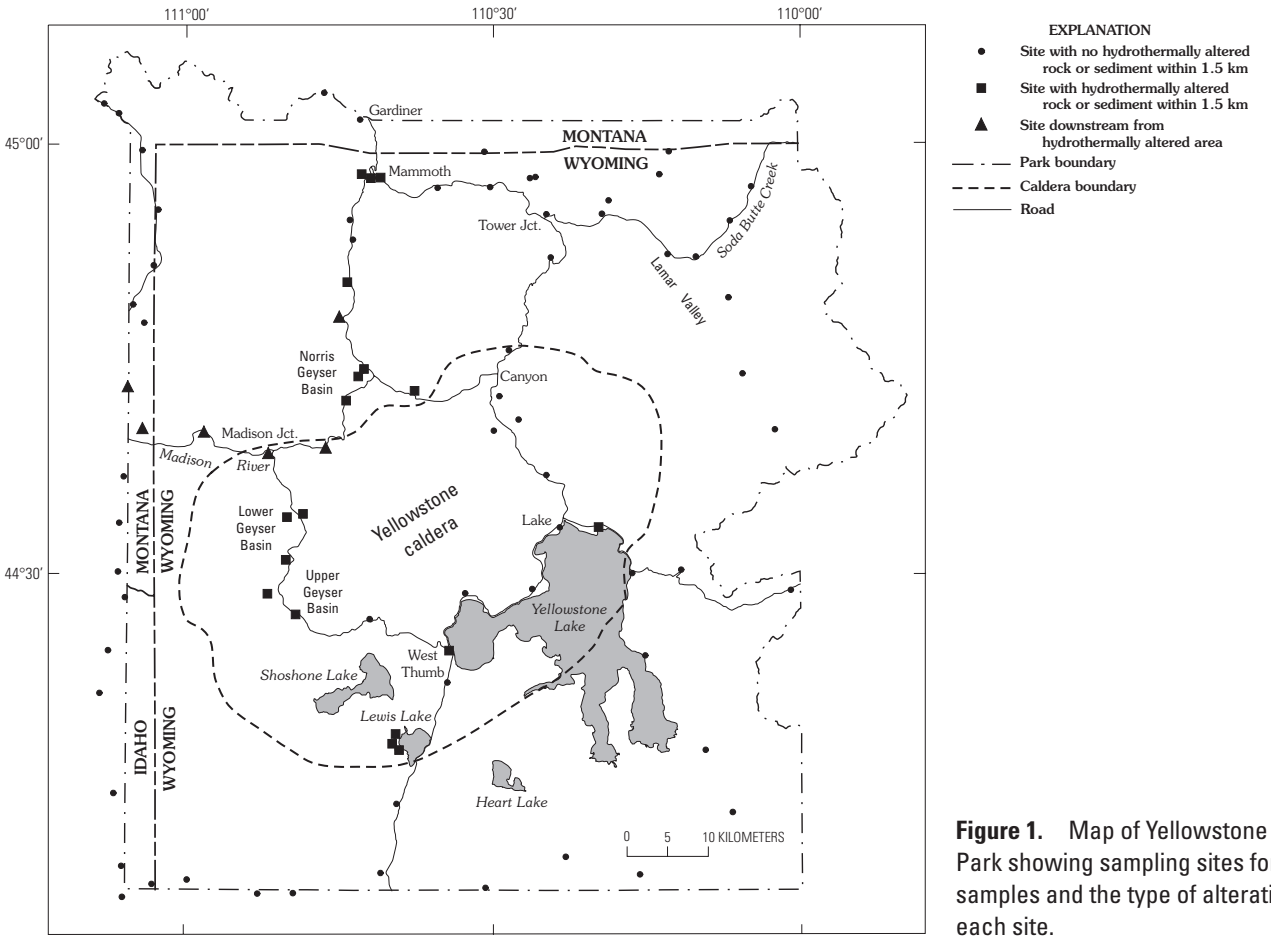

Figure 1. Map of Yellowstone National Park showing sampling sites for scat samples and the type of alteration for each site.

Collection, Preparation, and Analysis of Samples

The geology of Yellowstone National Park is complex and is discussed in detail in Christiansen (2001). Only a brief summary is included here. Further summaries are given in some of the papers in this volume. The oldest rocks in the Park consist mostly of Precambrian metasedimentary rocks that locally include quartz monzonite and diorite intrusions. These units crop out in several localities in the north-central part of the Park, generally north of the Lamar Valley (fig. 1). Paleozoic sedimentary rocks, composed mostly of quartzite, sandstone, and limestone, are found in scattered localities, mainly around the perimeter of the Park. Tertiary andesites are found mostly along the eastern perimeter of the Park. Quaternary felsic volcanic rocks crop out throughout much of the Park and are the most common rock type found. Deposits of Quaternary alluvium and glacial till locally cover all older units.

Figure 1 shows sites in the Park where scat samples were collected. These sites have been placed into the following groups: (1) sites containing generally fresh rock or sediment with no hydrothermally altered rock any closer than about 1.5 km of the plotted site (solid circles), (2) sites containing hydrothermally altered rock or sediment within about 1.5 km of the plotted site (solid squares), and (3) sites near streams but more than about 1.5 km downstream from any altered outcrops (solid triangles).

We collected 48 samples of bison scat, 67 samples of elk scat, and 2 samples of moose scat from 87 sites in and near Yellowstone National Park (fig. 1). At 29 of these sites, we collected both bison and elk scat. Each sample was composited (pooled) with material collected within a roughly 30-m (about 100-ft) radius of the plotted sample site. Care was taken to avoid including substrate material present underneath the scat. Most elk scat consisted of desiccated, winter pellets that were deemed to be as much as a year old but still appeared to be fresh with no obvious signs of decomposition. Bison scat was also relatively fresh. Most samples were desiccated; however, many were still moist. After drying, all scat material was pulverized to a coarse powder. Samples were analyzed in a random order. Internal standards and duplicate samples were also analyzed to monitor accuracy and precision.

In the laboratory, a sample aliquot was pelletized and analyzed for 35 elements (Ag, As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, K, La, Lu, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W, Yb, and Zn) by neutron activation analysis by Activation Laboratories, Ltd., Ancaster, Ontario, Canada. In addition, aliquots of the macerated material were combusted to ash in a muffle furnace to determine the amount of noncombustible (inorganic) material. This amount is defined as "percent ash." In the case of bison, elk, and moose scat, the organic material is composed largely of vegetable matter, and the inorganic material is composed mainly of grains of mineral matter in the soil attached to plant roots and of residue compounds, such as silica, that remain after ashing of certain plant species.

Results of Analyses

The results of the analyses are summarized in tables 1–3 for bison, elk, and moose scat, respectively. For some elements, some of the analyses were determined to be below the lower limit of determination (qualified analyses). Analyses in these tables shown as "unqualified" are those that the analysts reported as being above the lower limit of determination for the analytical method used.

Four elements (Ag, Hg, Ir, and Se) in the bison data set (table 1), five elements (Ag, Hg, Ir, Ni, and Se) in the elk data set (table 2), and 13 elements (Ag, Au, Cs, Eu, Hg, Ir, Nd, Ni, Se, Ta, Tb, U, and W) in the moose data set (table 3) did not have sufficient unqualified analyses in order to calculate a meaningful geometric mean value. The geometric mean values for elements in stream-sediment samples (table 1 in Chaffee, Carlson, and King, this volume) give a good estimate of the overall chemistry of surface mineral matter present in and near Yellowstone National Park and thus provide a context for the mean concentrations found in the scat samples. To determine which of 30 selected elements had unusual concentrations in the scat, we normalized geometric mean concentrations in the scat against those of the stream sediment. The resulting ratios, based on arbitrarily selected ratio threshold values, show relatively high values for an identical suite of 12 elements in both bison and elk scat. We did not have sufficient data to adequately evaluate element enrichment in moose scat. Elements with a ratio of ≥0.20 for bison scat include, in order of ratio value: Br (1.76), Zn (1.13), Mo (0.97), Ca (0.85), Sr (0.63), Cs (0.56), W (0.35), Sb (0.34), As (0.33), K (0.24), Ba (0.22), and Rb (0.20). Those with a ratio of ≥0.10 for elk scat include Zn (1.41), Br (1.31), Ca (0.99), Mo (0.50), Sr (0.49), Cs (0.20), Ba (0.18), K (0.17), Sb (0.16), Rb (0.16), As (0.14), and W (0.10). These 12 elements seem to fall into three groups: (1) hydrothermally related elements (As, Br, Cs, Mo, Sb, and W); (2) major elements (Ca and K), which are essential elements for plants, and trace elements (Ba, Rb, and Sr) that commonly proxy for Ca or K; and (3) zinc. The behavior of zinc is not known. It is an essential element for plants and animals but does not proxy for either Ca or K. Zinc is also not related to hydrothermal activity.

Published analyses (see, for example, King and others, 1984; Shacklette, 1972, 1980) indicate that the typical ash content for the above-ground parts of plants is in a range of about 3–7 percent. In contrast, the values for percent ash for the scat samples for bison and elk range from about 10 percent to more than 44 percent (tables 1 and 2). The values, although limited, for moose are about 4 percent (table 3). The amount of ash, which represents the amount of inorganic material in a sample, is thus much higher in the bison and elk scat samples than what would be expected if the animals consumed only above-ground plant material. However, some sedges and other types of plants growing in the vicinity of sinter-rich areas are known to contain a high natural ash content as a result of the high content of silica accumulated in these species (James Otton, written commun., 2001). Comparisons of the mean and maximum values for percent ash for bison and elk scat (tables 1 and 2) and the values for percent ash for the sample pairs from individual sites (not shown here) clearly indicate that bison ingest more mineral matter containing hydrothermal elements than do elk. Comparison of the geometric mean values for all samples for bison (25.5 percent) and elk (14.2 percent) (tables 1 and 2) indicates that the ash content for bison is roughly 1.8 times that of elk. The range of values for percent ash for each species suggests, however, that this ratio will vary in detail for sample pairs collected at a given site. Nevertheless, this value of 1.8 is a good first approximation of the general percent-ash contents between the two species. We think that the differences in ash content for each species reflect their foraging habits. Bison and elk, which mainly consume grasses, ingest significant quantities of mineral matter, most of which is probably soil material attached to plant-root masses. The percent-ash values for elk are generally lower than those for bison because elk probably consume a higher percentage of the above-ground parts of plants and therefore a lower percentage of soil mineral matter.

In contrast to the data for bison and elk, the two samples of moose scat show a very low percent ash, probably emphasizing their different diet. Moose mostly feed in wetlands and tend to be browsers rather than grazers. Their browse evidently contains much less soil substrate, surface contaminants, or plants with a high silica content.

Results of Factor Analysis

Variables selected from tables 1 and 2 were examined for covariance using R-mode factor analysis. Details concerning this mathematical treatment of analytical data are given in Chaffee, Carlson, and King (this volume). Of the original 36 variables determined for the bison and elk scat, 30 (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mo, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, W, Yb, Zn, and percent ash) were selected for factor analysis. Five elements were deleted from the data set prior to the factor analysis because each had very few or no unqualified values. Additionally, gold was deleted because the sample aliquots used for analysis were deemed to be too small to provide meaningful analyses.

Tables 4 and 5 show the factor loading values for bison and elk scat, respectively. Factor scores, also generated in the analysis but not tabulated for this report, give an indication of how well an individual sample correlates with a given factor. The distributions of samples with high factor scores can thus be used to identify any spatial relationship between the chemistry of a given sample and the various types of altered or unaltered rocks present near the sample site or upstream from the site.

For the bison samples (table 4) a four-factor model explains 84 percent of the total variance in the data set. Factor 1 contains variables (19 elements plus percent ash) associated with the overall chemistry of major rock units

Table 1. Summary statistics for analyses of 36 variables in 48 samples of bison scat, Yellowstone National Park and vicinity.

[Concentrations are shown in dry weight and in ppm, unless "(ppb)" or "(%)" shown after element symbol. N, not detected at the lower limit of determination shown in parentheses. Mean values based on unqualified values only. "---" in geometric mean column indicates no meaningful value]

Element	Range of values		Number unqualified	Percent unqualified	Geometric mean
	Minimum	Maximum			
Ag	N(0.3)	N(0.3)	0	0	---
As	0.33	18	48	100	2.0
Au (ppb)	N(0.10)	3.9	42	88	0.66
Ba	84	490	48	100	170
Br	2.6	10	48	100	5.1
Ca (%)	0.68	3.60	48	100	1.37
Ce	1.4	28	48	100	9.3
Co	0.3	6.1	48	100	1.3
Cr	1.4	63	48	100	9.4
Cs	0.28	20	48	100	2.0
Eu	N(0.05)	0.44	46	96	0.12
Fe (%)	0.055	1.27	48	100	0.33
Hf	0.11	2.6	48	100	0.90
Hg	N(0.05)	0.73	2	4	---
Ir (ppb)	N(0.10)[1]	N(0.10)[1]	0	0	---
K (%)	N(0.05)	1.20	46	96	0.51
La	0.91	19	48	100	5.8
Lu	0.006	0.19	48	100	0.05
Mo	N(0.05)	15	47	98	3.3
Na	220	6,500	48	100	1,800
Nd	0.60	11	48	100	3.3
Ni	N(2)	18	9	19	8.4
Rb	5.0	37	48	100	17
Sb	0.048	3.1	48	100	0.23
Sc	0.16	4.1	48	100	0.95
Se	N(0.10)	0.50	5	10	---
Sm	0.12	1.8	48	100	0.59
Sr	N(10.)	280	40	83	120
Ta	N(0.05)	0.42	33	69	0.16
Tb	N(0.10)	0.30	25	52	0.15
Th	0.10	3.8	48	100	1.2
U	N(0.01)	1.1	46	96	0.34
W	N(0.05)	44	30	63	2.6
Yb	0.059	1.27	48	100	0.38
Zn	33	160	48	100	79
Ash (%)	18.2	44.0	48	100	25.5

[1]Lower limit of determination reported as 0.20 for 17 samples.

(mainly unaltered rhyolites and andesites) exposed in the Park. Samples strongly correlated with this factor are from sites located throughout the study area and are not closely related to any one geologic unit. Percent ash is most strongly loaded on this factor, reflecting a close association between ash content and the chemistry of rock material included in bison scat.

Factor 2 contains elements associated with chemical enrichment related to hydrothermal activity (Cs, W, Sb, As, Br, and Mo). Samples strongly correlated with this factor are mainly from hydrothermally altered areas in geyser basins or hot-spring areas, or from localities immediately downstream from these features.

Factor 3 contains only zinc. A zinc factor is also present for the elk samples (table 5). The reason for zinc not being associated with variables in other factors is not clear. Factor scores do not indicate that there is any close association of samples containing anomalous zinc with any particular geologic unit. As noted previously, zinc seems to be enriched in scat as compared to stream sediment, and its chemical affinity is not clearly understood. We speculate that bison and elk may metabolize zinc differently than they do other elements.

Table 2. Summary statistics for analyses of 36 variables in 67 samples of elk scat, Yellowstone National Park and vicinity.

[Concentrations are shown in dry weight and in ppm, unless "(ppb)" or "(%)" shown after element symbol. N, not detected at the lower limit of determination shown in parentheses. Mean values based on unqualified values only. "---" in geometric mean column indicates no meaningful value]

Element	Range of values		Number unqualified	Percent unqualified	Geometric mean
	Minimum	Maximum			
Ag	N(0.3)	N(0.3)	0	0	---
As	0.10	18	67	100	0.83
Au (ppb)	N(0.10)	7.7	57	85	0.59
Ba	60	280	67	100	140
Br	1.5	20	67	100	3.8
Ca (%)	0.67	3.40	67	100	1.60
Ce	0.8	22	67	100	4.8
Co	0.40	2.3	67	100	0.83
Cr	0.90	14	67	100	3.9
Cs	0.12	19	67	100	0.72
Eu	N(0.05)	0.19	40	60	0.08
Fe (%)	0.05	0.53	67	100	0.15
Hf	N(0.05)	2.3	66	99	0.44
Hg	N(0.05)	0.24	2	3	---
Ir (ppb)	N(0.10)[1]	N(0.10)[1]	0	0	---
K (%)	N(0.05)	1.70	66	99	0.37
La	0.66	14	67	100	3.6
Lu	0.003	0.185	67	100	0.027
Mo	0.23	12	67	100	1.7
Na	180	3,800	67	100	730
Nd	N(0.5)	8.7	66	99	2.0
Ni	N(2)	6.0	3	4	---
Rb	2.0	67	67	100	13
Sb	0.029	8.2	67	100	0.11
Sc	0.12	1.8	67	100	0.43
Se	N(0.10)	0.60	8	12	---
Sm	0.05	1.4	67	100	0.33
Sr	N(10.)	320	61	91	94
Ta	N(0.05)	0.38	31	46	0.10
Tb	N(0.10)	0.30	13	19	0.12
Th	N(0.10)	2.6	66	99	0.55
U	N(0.01)	0.85	61	91	0.16
W	N(0.05)	24	38	57	0.74
Yb	0.23	1.2	67	100	0.19
Zn	49	270	67	100	99
Ash (%)	5.1	28.6	66	99	14.2

[1]Lower limit of determination reported as 0.20 for 12 samples.

Zinc may also be concentrated in their forage. However, other undefined factors may also be involved.

Factor 4 is strongly loaded with calcium and potassium. This factor may be related to alkali and alkaline-earth elements commonly enriched in plants. Factor scores do not reveal a close spatial association with any particular geologic substrate.

Table 5 shows the factor loading values for a five-factor model for the elk samples. This model explains 81 percent of the variance in the data set. Variables strongly loaded on factors 1 and 4 include those related to lithology. Loading values and factor scores indicate that factor 1 (Sc, Fe, Cr, Na, percent ash, Eu, Co, Hf, Th, and U) is most closely associated with samples from areas containing andesitic volcanic rocks, which crop out mostly in the northern and eastern parts of the Park. Factor 4 (La, Sm, Nd, Ce, Lu, Yb, Th, Hf, Tb, Ta, Eu, and Ba) is more closely associated with samples from areas of rhyolitic volcanic rocks, which are most commonly found in the central, southern, and western parts of the Park.

Factor 2 (W, Cs, As, Sb, Mo, and Br) is associated with elements enriched in altered rocks from areas of past or present hydrothermal activity. Samples with high scores for this

Table 3. Summary statistics for analyses of 36 variables in 2 samples of moose scat, Yellowstone National Park and vicinity.

[Concentrations are shown in dry weight and in ppm, unless "(ppb)" or "(%)" shown after element symbol. N, not detected at the lower limit of determination shown in parentheses. Mean values based on unqualified values only. "---" in geometric mean column indicates no meaningful value]

Element	Range of values		Number unqualified	Percent unqualified	Geometric mean
	Minimum	Maximum			
Ag	N(0.3)	N(0.3)	0	0	---
As	0.20	0.21	2	100	0.20
Au (ppm)	N(0.10)	0.80	1	50	---
Ba	150	190	2	100	170
Br	1.5	2.4	2	100	1.9
Ca (%)	0.89	1.40	2	100	1.12
Ce	0.9	0.9	2	100	0.9
Co	0.30	0.50	2	100	0.39
Cr	1.7	1.8	2	100	1.7
Cs	0.06	0.14	2	100	0.09
Eu	N(0.05)	N(0.05)	0	0	---
Fe (%)	0.04	0.05	2	100	0.04
Hf	0.09	0.14	2	100	0.11
Hg	N(0.05)	N(0.05)	0	0	---
Ir (ppb)	N(0.10)	N(0.10)	0	0	---
K (%)	0.11	0.12	2	100	0.11
La	0.51	0.53	2	100	0.52
Lu	0.006	0.006	2	100	0.006
Mo	0.26	0.29	2	100	0.27
Na	120	160	2	100	140
Nd	N(0.5)	N(0.5)	0	0	---
Ni	N(2)	N(2)	0	0	---
Rb	2.0	3.0	2	100	2.4
Sb	0.035	0.038	2	100	0.036
Sc	0.12	0.13	2	100	0.12
Se	N(0.10)	0.2	1	50	---
Sm	0.05	0.06	2	100	0.05
Sr	40	70	2	100	53
Ta	N(0.05)	N(0.05)	0	0	---
Tb	N(0.1)	N(0.1)	0	0	---
Th	0.10	0.10	2	100	0.10
U	N(0.01)	0.03	1	50	---
W	N(0.05)	0.52	1	50	---
Yb	0.032	0.041	2	100	0.036
Zn	160	180	2	100	170
Ash (%)	3.8	4.3	2	100	4.0

factor show a close spatial correlation with sites near hydrothermally altered areas. Factor 3 is loaded with alkali and alkaline-earth elements (K, Ca, Rb, and Sr), which are most commonly associated with major rock-forming minerals but also may be enriched in plant ash. However, samples with high factor scores for this factor do not show a close spatial association with any one geologic unit.

Factor 5 is loaded primarily with zinc and secondarily with cobalt. This segregation of zinc was previously identified in the bison factor analysis. Samples with high scores for this factor also do not show a close spatial correlation with any one rock unit.

Distributions of Anomalies for Selected Variables

Figures 2–9 show the distributions of anomalies for selected variables in scat samples. The threshold values for each animal species and variable were selected after examining histograms showing concentration distributions and plots of values for each variable. For most variables, the histograms show a single population, suggesting a single source for that variable. For those variables, approximately the top 30 percent of the values were deemed anomalous. Arsenic, however, seems to be distributed bimodally, but the two populations are

not easily separated. Consequently, the top 30 percent of the values is anomalous for arsenic as well. Zinc shows a much clearer bimodal distribution, suggesting two separate sources for this element. The threshold selected for zinc includes most of the samples in the population with the higher concentrations. Thus, 40 percent of the bison scat samples and 52 percent of the elk samples are anomalous for zinc.

Figure 2 shows the distribution of anomalous lanthanum (>7.0 ppm in bison scat; >4.6 ppm in elk scat). Lanthanum is a trace element commonly found in rocks in rock-forming accessory minerals. This element is strongly loaded on factor 1 for bison scat (table 4) and factor 4 for elk scat (table 5). Both of these factors are chemically related to rock lithology.

The highest lanthanum concentrations are found in scat from areas of both fresh and hydrothermally altered rock, mainly in the widespread rhyolites that crop out in the central, southern, and western parts of the Park. It is also enriched locally in a few samples from areas of unaltered rocks in the northern and eastern part of the Park that are underlain by Tertiary andesites, Precambrian metamorphic rocks, or Paleozoic sedimentary rocks (Chaffee, Carlson, and King, this volume; Christiansen, 2001). Lanthanum in scat is anomalous in hydrothermally altered areas, such as the Upper, Lower, and Norris Geyser Basins, and also in localities where no geothermal activity has occurred, such as in the northern part of the Park, between Mammoth and Soda Butte Creek.

Table 6 shows the percentage of sample sites with anomalies for selected elements. Elements with a high percentage of anomalous samples from altered sites are clearly related to hydrothermal activity. The data in table 6 indicate that only a minority of samples from either altered or unaltered sites are anomalous for lanthanum or zinc, emphasizing the fact that these elements are not closely associated with hydrothermal activity. Anomalies of lanthanum in hydrothermal areas are therefore largely the result of primary rock chemistry and not the overprinting of elements enriched in hydrothermal fluids. This conclusion has also been demonstrated mathematically by applying factor analysis to chemical data sets composed of rock and (or) stream-sediment samples collected Park-wide (Chaffee, Carlson, and King, this volume). Lanthanum is not an essential element for animal nutrition (Gough and others, 1979). Its concentration in scat samples is probably related to inorganic material ingested along with plant matter. Individual samples of bison and elk tissue from Park animals were analyzed for this study. Both contained 1.5 ppm La (table 7)

Figure 3 shows the distribution of cesium in scat samples. Cesium is a trace element whose distribution in rocks of the Yellowstone area is closely associated with hydrothermal activity (Chaffee, Carlson, and King, this volume). Cesium commonly proxies for potassium in minerals such as feldspars and micas. Sites whose samples contain anomalous cesium (>3.8 ppm, bison; >1.0 ppm, elk) (fig. 3) are commonly located near or downstream from hydrothermally affected areas (fig. 1). From 79–94 percent of the samples from altered sites contain anomalous cesium (table 6), whereas only 4 percent of the samples from nonaltered sites are anomalous.

Table 4. Factor-loading values for 30 variables in 48 samples of bison scat, Yellowstone National Park and vicinity.

[Four-factor model, varimax loading, based on log-normalized values]

Factor 1 (lithology)		Factor 2 (hydrothermal)		Factor 3 (zinc)		Factor 4 (alkali metals and alkaline earths)	
La	0.97	Cs	0.86	Zn	0.78	K	0.70
Ce	0.97	W	0.86			Ca	0.55
Sm	0.97	Sb	0.84				
Hf	0.96	As	0.81				
Nd	0.95	Br	0.81				
Na	0.93	Mo	0.66				
Yb	0.93	Sr	–0.87				
Th	0.93						
Eu	0.89						
Lu	0.85						
U	0.82						
Fe	0.78						
Tb	0.77						
Rb	0.71						
Sc	0.69						
Ta	0.65						
%Ash	0.65						
Co	0.63						
Cr	0.60						
Ba	0.58						
Percent variability explained							
49%		27%		4%		4%	

The highest cesium concentrations are in scat samples collected near hydrothermal areas in the Upper and Lower Geyser Basins, south of Madison Junction, and near Norris Geyser Basin. Studies of cesium radionuclides (see, for example, Hakonson, 1967) indicate that cesium is most commonly concentrated in muscle tissue. However, it is probably not an essential element for animals. Samples of bison and elk tissue from Park animals contained 0.25 ppm Cs and 1.3 ppm Cs, respectively (table 7). Kabata-Pendias (2001) showed that cesium is not an essential component of plant tissue.

Figure 4 shows the distribution of anomalous arsenic (>2.7 ppm, bison; >1.0 ppm, elk) in scat. Arsenic is abundant in the thermal waters in Yellowstone (Ball and others, 1998; Miller and others, 1997; Thompson and DeMonge, 1996) and is present in anomalous concentrations in water, sinter deposits, and stream sediment in most areas affected by thermal activity. The mineral residence of arsenic in the Park is uncertain, but it is probably present in sulfur-rich minerals, such as pyrite or native sulfur. The spatial correlation of arsenic anomalies in scat with sites near or downstream from hydrothermally altered areas is similar to that of cesium. High percentages of the samples from altered sites contain anomalous arsenic (table 6), and only 4–8 percent

Table 5. Factor-loading values for 30 variables in 67 samples of elk scat, Yellowstone National Park and vicinity.

[Five-factor model, varimax loading, based on log-normalized values. Elements in italics are secondary loading values]

Factor 1 (mafic rocks)		Factor 2 (hydrothermal)		Factor 3 (alkali metals and alkaline earths)		Factor 4 (felsic rocks)		Factor 5 (zinc)	
Sc	0.94	W	0.88	K	0.87	La	0.94	*Co*	*0.56*
Fe	0.91	Cs	0.86	Ca	0.76	Sm	0.93	Zn	0.52
Cr	0.91	As	0.84	Rb	0.72	Nd	0.93		
Na	0.75	Sb	0.84	Sr	0.56	Ce	0.87		
%Ash	0.75	Mo	0.67			Lu	0.85		
Eu	0.72	Br	0.67			Yb	0.84		
Co	0.68					Th	0.67		
Hf	0.56					Hf	0.66		
Th	0.56					Tb	0.59		
U	0.46					Ta	0.56		
						Eu	*0.49*		
						Ba	0.41		
Percent variability explained									
42%		17%		10%		8%		4%	

of the samples from nonaltered sites are anomalous, emphasizing the strong hydrothermal association of this element. Like cesium, the highest arsenic concentrations are found in samples collected in the Upper and Lower Geyser Basins, south of Madison Junction, near Norris Geyser Basin, and in the Mammoth Hot Springs area. Other anomalies are present at scattered localities, mainly near active thermal areas (fig. 4). Few arsenic analyses of tissue from large animals found in the Park are available. However, a sample of bison tissue analyzed for this study contained 0.3 ppm As and a sample of elk tissue, 0.4 ppm As (table 7). No analyses were determined for moose in the Park. Studies conducted elsewhere indicate that arsenic is concentrated in animal organs such as livers and kidneys (Puls, 1988). In very small concentrations, arsenic is considered a necessary element for animals. High concentrations of arsenic tend to enhance the toxic effects of selenium in animals (Speidel and Agnew, 1982). In human beings, arsenic can be carcinogenic (Gough and others, 1979). Toxic levels for the large Park animals, and the eventual long-term effects of ingestion of arsenic by these animals, are not known.

Figure 5 shows the distribution of anomalous molybdenum (>3.9 ppm, bison; >2.4 ppm, elk) in the scat samples. Anomalous molybdenum is found in most of the samples collected from sites associated with geothermal activity (fig. 1). Like cesium and arsenic, molybdenum is anomalous in a high percentage of samples from altered sites (table 6) and is anomalous in only a small percentage of samples from nonaltered sites, indicating a strong association with geothermal activity. The highest molybdenum concentrations are found in samples from the Upper and Lower Geyser Basins and Norris Geyser Basin. Factor analysis studies of molybdenum in sediment samples (Chaffee, Carlson, and King, this volume) also indicate that this element is associated with geothermal activity. However, unlike arsenic, molybdenum also exhibits a strong lithologic association, mainly with the felsic volcanic rocks but also locally with other lithologies. The mineral residence of molybdenum in the Yellowstone area is not known.

Molybdenum is known to be present in high concentrations in some plant species (Gough and others, 1979). At low concentration levels, it is an essential element for animals. Individual samples of bison and elk tissue from Park animals both contained <0.1 ppm Mo (table 7). Studies of domestic livestock have shown that molybdenum ingested in relatively large amounts over a long period of time can, under certain conditions, be toxic, particularly where available copper concentrations in the food are very low or sulfur concentrations are very high (Gough and others, 1979; Puls, 1988). Whether these conditions exist in terms of forage for animals in Yellowstone is not known.

The distributions of anomalous zinc (>85 ppm, bison; >100 ppm, elk) are shown in figure 6. Zinc is an essential nutrient for both plants and animals (Gough and others, 1979; Puls, 1988). Although rare, high (>5,000 ppm) concentrations of zinc in the diet of cattle may be toxic (Puls, 1988). Samples of bison and elk tissue analyzed for this study contained 210 ppm and 112 ppm, respectively (table 7). Zinc is a common trace constituent in iron- and magnesium-rich rock-forming accessory minerals and is highly mobile in many weathering environments. Both factor

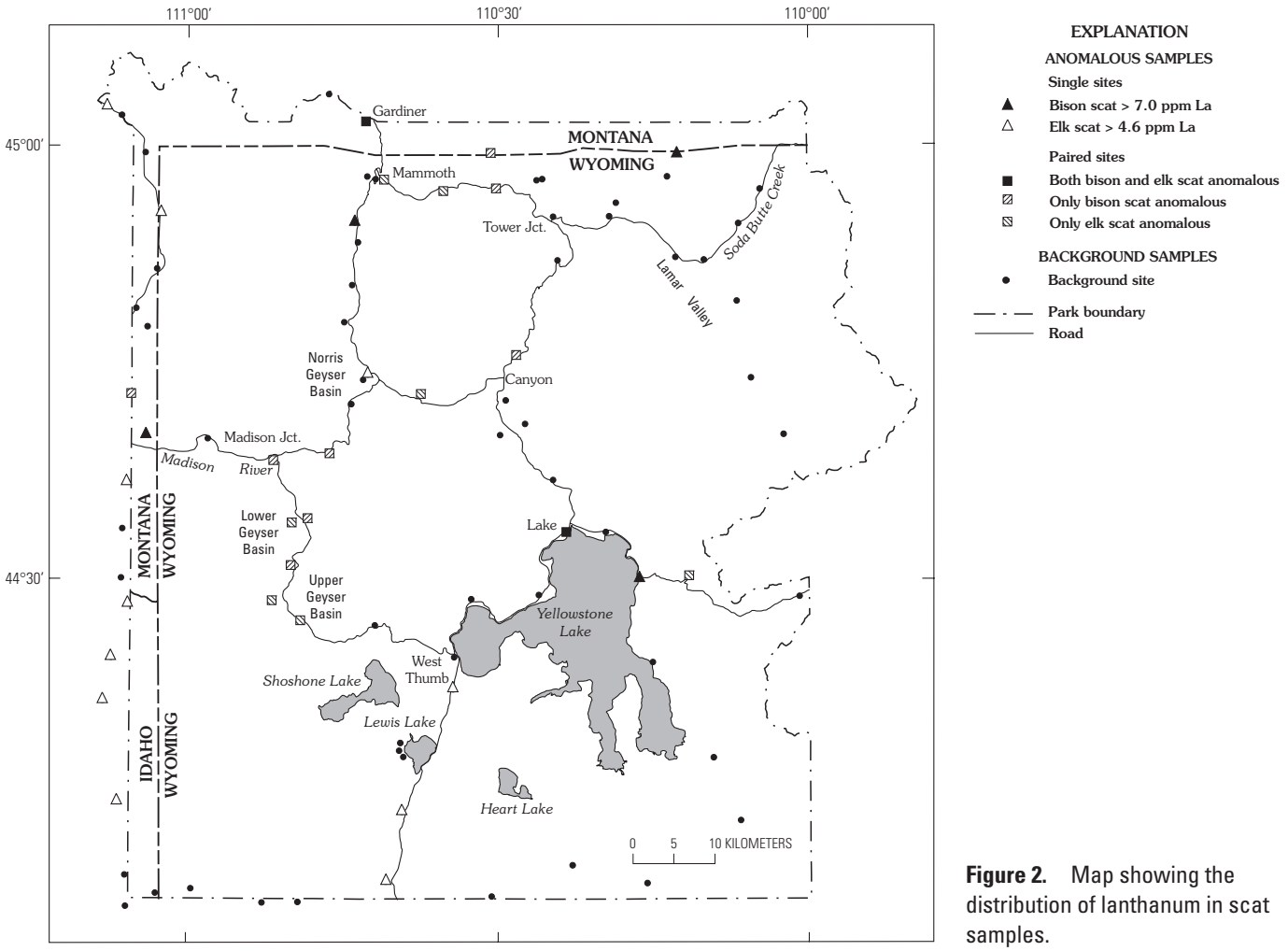

Figure 2. Map showing the distribution of lanthanum in scat samples.

Table 6. Percentage of scat sample sites with anomalies for selected elements.

Element	Altered sites		Nonaltered sites	
	Bison sites (%)	Elk sites (%)	Bison sites (%)	Elk sites (%)
La	42	39	25	27
Cs	79	94	4	4
As	68	89	4	8
Mo	74	83	4	10
Zn	58	78	32	47

analyses (tables 4 and 5) classify zinc separately from most of the other variables.

Although a majority of the samples collected from altered sites contain anomalous zinc (table 6), a relatively high percentage of samples from nonaltered sites are also anomalous, emphasizing that zinc behaves differently from the other elements discussed here. Zinc is not closely associated chemically with hydrothermal activity in the Park.

Anomalous zinc is present in bison scat collected from scattered localities between the Upper and Norris Geyser Basins and the Park boundary near the town of West Yellowstone, near Yellowstone Lake, along the Yellowstone River near Canyon, and in the Mammoth-Gardiner (Mont.) area. In contrast, samples of elk scat with anomalous zinc are generally confined to the southern and western parts of the study area. The two moose samples are strongly anomalous (160 ppm and 180 ppm Zn, respectively), suggesting that moose are consuming plants that have relatively high concentrations of zinc. Analyses of moose pellets from Alaska (Day and others, 1985) show consistently high zinc concentrations, confirming our observations in Yellowstone.

Concentrations of zinc for both bison and elk scat exhibit a bimodal distribution, suggesting two sources for this element. We speculate that one source is ingested plant material and the other is inorganic rock material attached to

Table 7. Composition of biological samples from Yellowstone Lake and the greater Yellowstone ecosystem.

[All units are ppm. Leaders (---) indicate no data]

Sample type	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe
Gill-net macrophytes	< 0.01	90	2.8	8.4	0.32	< 0.005	560	0.03	0.74	0.07	---	1.1	0.4	120
Algal pod	< 0.01	40	1.8	3.2	< 0.01	0.01	1,100	0.04	0.69	0.12	---	0.12	< 3	110
Mat from above vent	0.01	500	6.3	16	0.98	0.01	300	< 0.01	5.3	0.18	---	6.8	< 3	340
60-µm near shore	< 0.01	380	7.9	6.3	0.28	0.02	400	0.03	9.6	0.26	---	2.7	0.8	350
Plankton- 243 µm	< 0.01	50	7.2	6.5	< 0.01	< 0.005	2,700	0.04	0.16	0.09	---	2.5	0.6	70
Plankton- 11µm at 1m	0.02	220	5.2	5.6	0.06	0.02	1,600	0.32	0.87	1.5	---	1.3	11	710
Trout														
Average cutthroat trout stomach contents	< 0.02	681	15	161	0.088	0.013	38,605	0.21	---	0.53	2.1	28.2	39.1	1,008
Average lake trout stomach contents	< 0.02	1,861	46	278	0.247	0.035	26,013	1.55	---	1.31	3.2	18.5	33.1	3,433
Average spawning cutthroat trout muscle	< 0.02	45.0	0.57	9.7	0.003	0.005	8,373	0.03	< 0.5	0.13	2.7	26.2	4.7	107
Average cutthroat trout muscle	<0.02	< 8	0.23	< 0.5	< 0.001	< 0.005	2,201	< 0.003	< 0.5	< 0.1	8.6	83.0	4.6	< 50
Average lake trout muscle	< 0.02	< 8	1.4	< 0.5	< 0.001	< 0.005	2,492	0.006	< 0.5	< 0.1	10.5	69.3	3.7	< 50
Average cutthroat trout liver	< 0.02	24.6	2.0	0.59	0.013	0.030	441	0.49	---	0.30	0.2	21.0	496.3	1,142
Average lake trout liver	< 0.02	15.4	9.6	0.94	0.001	0.015	361	1.36	---	0.57	0.1	13.8	56.3	973
Plants														
Pine nut	< 0.02	46.2	< 0.1	< 0.5	< 0.001	0.006	75.0	0.09	< 0.5	0.11	2.7	0.02	10.9	< 50
Pine nut	< 0.02	< 8	< 0.1	< 0.5	< 0.001	< 0.005	34.5	0.1	< 0.5	< 0.1	0.86	0.02	4.9	< 50
Pine nut	< 0.02	40.8	< 0.1	< 0.5	< 0.001	< 0.005	47.1	0.08	< 0.5	0.13	1.5	0.02	6.4	< 50
Pine nut	< 0.02	20.1	< 0.1	< 0.5	< 0.001	< 0.005	41.7	0.05	< 0.5	< 0.1	1.2	0.01	4.3	< 50
Pine nut	< 0.02	58.8	< 0.1	< 0.5	< 0.001	< 0.005	69.3	0.12	< 0.5	< 0.1	1.6	0.02	8.7	< 50
Pine nut	< 0.02	35.6	< 0.1	< 0.5	< 0.001	< 0.005	49.7	0.08	< 0.5	< 0.1	1.4	0.02	9.5	< 50
Equisetum	0.02	32.9	< 0.1	24.3	0.008	0.02	5,020	1.9	< 0.5	0.23	1.5	0.24	10.8	110
Clover	< 0.02	63.6	< 0.1	39.5	0.002	0.007	3,140	0.007	< 0.5	0.27	0.77	0.004	3.7	130
Perodecidia gairdnew	< 0.02	332	0.2	24.0	0.02	0.01	884	0.30	0.98	0.14	1.6	0.05	7.8	310
Heracleum	< 0.02	125	< 0.1	52.1	0.001	0.006	5,490	0.08	< 0.5	0.22	1.2	0.02	7.3	210
Cirsuim scariagm	< 0.02	55.5	< 0.1	197	0.005	< 0.005	3,080	0.10	< 0.5	< 0.1	1.2	0.02	2.1	60
Animals														
Bison flesh	< 0.02	10.7	0.3	0.58	0.003	0.006	107	0.006	< 0.5	< 0.1	2.3	0.25	5.7	190
Mule deer flesh	< 0.02	16.2	< 0.1	< 0.5	< 0.001	0.005	177	0.08	< 0.5	< 0.1	2.1	0.03	16.1	160
Elk flesh	< 0.02	< 8	0.4	< 0.5	0.004	0.005	86.3	0.006	< 0.5	< 0.1	1.8	1.3	6.2	110
Hayden Valley grizzly bear flesh	< 0.02	< 8	< 0.1	< 0.5	0.005	< 0.005	159	0.04	< 0.5	< 0.1	2.0	0.35	7.5	230
Gallatin NF grizzly bear flesh	< 0.02	7.9	< 0.1	< 0.5	0.002	< 0.005	133	0.05	< 0.5	< 0.1	2.0	0.09	7.3	300
Gallatin NF grizzly bear hair	< 0.02	202	< 0.1	10.0	< 0.001	0.02	639	0.11	< 0.5	< 0.1	2.2	0.04	11.4	140
Shoshone NF grizzly bear hair	0.18	452	0.1	7.3	0.02	0.18	356	0.02	0.75	0.55	2.9	0.05	13.6	740
Yellowstone Lake grizzly bear hair	0.05	297	0.5	7.3	< 0.001	0.09	627	0.06	0.66	0.33	8.3	0.30	12.4	600
Yellowstone Lake grizzly bear hair	< 0.02	140	0.1	2.2	0.003	0.02	219	0.02	< 0.5	< 0.1	3.2	0.04	9.3	120

Table 7. Composition of biological samples from Yellowstone Lake and the greater Yellowstone ecosystem—*Continued*.

Sample type	Ga	Hg	K	La	Li	Mg	Mn	Mo	Na	Nb	Ni	P	Pb
Gill-net macrophytes	< 0.01	---	610	0.5	0.8	190	22	0.28	100	0.05	0.96	230	0.22
Algal pod	< 0.01	---	180	0.41	0.61	320	9.4	0.13	170	0.01	2.2	110	0.13
Mat from above vent	< 0.01	---	190	2.8	3.5	910	29.0	0.09	120	0.04	1	140	0.84
60-µm near shore	< 0.01	---	60	4.7	1.2	280	17.0	0.13	40	0.08	0.42	30	3.7
Plankton- 243 µm	< 0.01	< 0.2	2,000	0.09	28	1,400	3.2	0.98	6,500	0.01	0.67	1,200	0.46
Plankton- 11µm at 1m	< 0.01	< 0.2	710	0.44	9.9	710	18.0	0.49	3,600	0.01	590	360	15
						Trout							
Average cutthroat trout stomach contents	0.43	0.82	10,343	---	1.2	1,552	273	0.6	5,225	< 2	3.0	11,925	0.7
Average lake trout stomach contents	1.23	1.19	9,400	---	1.8	1,352	423	0.8	4,587	< 2	4.0	11,867	2.0
Average spawning cutthroat trout muscle	0.21	0.99	16,417	0.15	0.4	1,237	5.6	< 0.1	3,522	< 2	1.3	20,500	0.1
Average cutthroat trout muscle	0.026	0.9	44,698	< 0.3	< 0.2	2,852	1.6	< 0.1	7,161	< 2	< 1	26,199	< 0.2
Average lake trout muscle	0.023	0.9	42,880	< 0.3	< 0.2	2,774	0.9	< 0.1	7,982	< 2	< 1	24,949	< 0.2
Average cutthroat trout liver	0.09	1.56	13,965	---	0.4	486	6.3	1.1	6,057	< 2	< 1	11,283	0.7
Average lake trout liver	0.09	2.10	10,603	---	0.2	688	14.7	0.3	4,743	< 2	< 1	11,000	0.1
						Plants							
Pine nut	0.06	0.006	8,720	< 0.3	< 0.2	1,780	150	< 0.1	12	< 2	9.1	5,500	< 0.2
Pine nut	0.02	0.006	3,750	< 0.3	< 0.2	818	55.1	< 0.1	7	< 2	< 1	2,300	< 0.2
Pine nut	0.03	0.005	6,860	< 0.3	< 0.2	1,230	88.0	< 0.1	11	< 2	1.8	3,600	< 0.2
Pine nut	0.02	0.005	3,560	< 0.3	< 0.2	857	72.1	0.2	7	< 2	< 1	2,400	0.2
Pine nut	0.03	0.006	7,960	< 0.3	< 0.2	1,280	90.7	< 0.1	10	< 2	2.2	3,500	< 0.2
Pine nut	0.04	0.006	6,920	< 0.3	< 0.2	1,470	96.0	< 0.1	9	< 2	2.0	4,200	< 0.2
Equisetum	0.07	0.028	---	< 0.3	< 0.2	4,240	44.2	0.32	236	< 2	1.1	6,600	5.4
Clover	0.03	0.004	23,200	< 0.3	< 0.2	2,000	33.3	0.48	30	< 2	< 1	1,700	0.2
Perodecidia gairdnew	0.2	<0.004	19,900	0.51	0.2	1,000	42.0	0.42	78	< 2	< 1	4,500	0.5
Heracleum	0.1	0.007	---	< 0.3	< 0.2	2,630	36.6	2.00	86	< 2	2.2	7,600	0.2
Cirsuim scariagm	0.03	<0.004	---	0.49	< 0.2	710	11.9	0.44	39	< 2	< 1	2,100	< 0.2
						Animals							
Bison flesh	0.1	<0.004	18,800	< 0.3	1.5	656	0.98	< 0.1	3,850	< 2	< 1	9,400	< 0.2
Mule deer flesh	0.09	0.005	14,800	< 0.3	< 0.2	956	1.10	< 0.1	3,100	< 2	< 1	9,500	0.2
Elk flesh	0.08	0.008	13,700	< 0.3	1.5	978	0.63	< 0.1	1,670	< 2	< 1	8,900	< 0.2
Grizzly bear flesh	0.07	0.006	11,000	< 0.3	< 0.2	748	0.87	< 0.1	5,330	< 2	< 1	7,600	< 0.2
Grizzly bear flesh	0.09	0.014	19,400	< 0.3	< 0.2	1,080	0.89	0.1	2,510	< 2	< 1	11,000	< 0.2
Grizzly bear hair	0.06	0.09	518	< 0.3	< 0.2	466	21.4	0.1	220	< 2	< 1	330	0.50
Grizzly bear hair	0.2	0.08	258	0.33	< 0.2	538	18.0	0.2	315	5.6	1.1	270	0.58
Grizzly bear hair	0.1	0.61	2,680	0.35	< 0.2	344	7.9	0.23	952	< 2	1.6	880	1.4
Grizzly bear hair	0.05	1.7	122	< 0.3	< 0.2	103	4.1	< 0.1	124	< 2	< 1	240	0.59

Table 7. Composition of biological samples from Yellowstone Lake and the greater Yellowstone ecosystem—*Continued*.

Sample type	Rb	Sb	Sc	Se	Sr	Ta	Th	Ti	Tl	U	V	Y	Zn
Gill-net macrophytes	1.5	0.55	< 0.05	< 0.1	5	< 0.01	0.02	<10	0.02	0.04	0.4	0.39	15
Algal pod	0.3	0.02	< 0.05	< 0.1	6.9	< 0.01	0.03	<10	< 0.01	0.01	0.2	0.23	1
Mat from above vent	2.3	0.53	< 0.05	< 0.1	6.3	< 0.01	0.25	<10	0.02	0.11	0.4	1.4	3
60-µm near shore	1.1	0.05	0.1	< 0.1	4.1	< 0.01	1.4	<10	0.02	0.14	0.3	2.5	3
Plankton- 243 µm	8	0.23	< 0.05	0.1	23	< 0.01	< 0.005	<10	< 0.01	0.009	0.6	0.08	13
Plankton- 11 µm at 1m	2.3	0.04	0.07	< 0.1	13	< 0.01	0.04	<10	< 0.01	0.05	0.5	0.29	690
Trout													
Average cutthroat trout stomach contents	64.4	< 0.02	---	3.5	293	---	---	26.8	0.158	0.09	1.7	---	159
Average lake trout stomach contents	43.7	< 0.02	---	4.7	199	---	---	63.3	0.300	0.18	5.1	---	276
Average spawning cutthroat trout muscle	64.8	< 0.02	< 0.3	1.4	56	< 0.2	0.043	< 40	0.087	0.01	0.9	< 0.3	44.9
Average cutthroat trout muscle	201.5	< 0.02	< 0.3	2.9	10.1	< 0.2	< 0.03	< 40	0.15	< 0.02	< 0.4	< 0.3	85.5
Average lake trout muscle	167.2	< 0.02	< 0.3	4.1	8.9	< 0.2	< 0.03	< 40	0.21	< 0.02	< 0.4	< 0.3	26.1
Average cutthroat trout liver	79.0	< 0.02	---	7.5	1.3	---	---	< 40	0.733	0.02	1.2	---	117
Average lake trout liver	56.5	< 0.02	---	9.6	1.6	---	---	< 40	1.900	0.01	1.3	---	98.4
Plants													
Pine nut	22.7	< 0.02	< 0.3	< 0.2	0.09	< 0.2	0.18	< 40	< 0.003	< 0.02	0.5	< 0.3	47.1
Pine nut	4.9	< 0.02	< 0.3	< 0.2	< 0.05	< 0.2	0.04	< 40	< 0.003	< 0.02	< 0.4	< 0.3	30.1
Pine nut	16.9	< 0.02	< 0.3	< 0.2	0.05	< 0.2	0.06	< 40	< 0.003	< 0.02	< 0.4	< 0.3	34.4
Pine nut	12.6	< 0.02	< 0.3	< 0.2	0.08	< 0.2	0.04	< 40	< 0.003	< 0.02	< 0.4	< 0.3	23.0
Pine nut	6.6	< 0.02	< 0.3	< 0.2	0.20	< 0.2	0.03	< 40	< 0.003	< 0.02	< 0.4	< 0.3	47.8
Pine nut	8.7	< 0.02	< 0.3	< 0.2	0.06	< 0.2	< 0.03	< 40	< 0.003	< 0.02	< 0.4	< 0.3	41.4
Equisetum	65.8	< 0.02	0.3	< 0.2	126	0.43	1.2	< 40	0.007	< 0.02	0.4	< 0.3	55.9
Clover	3.1	< 0.02	< 0.3	< 0.2	105	< 0.2	0.25	< 40	0.003	< 0.02	< 0.4	< 0.3	9.6
Perodecidia gairdnew	7.6	< 0.02	< 0.3	< 0.2	17.0	0.22	0.59	< 40	0.008	< 0.02	0.8	< 0.3	24.5
Heracleum	23.3	< 0.02	< 0.3	< 0.2	134	< 0.2	0.15	< 40	0.004	< 0.02	0.6	< 0.3	28.6
Cirsuim scariagm	40.5	< 0.02	< 0.3	< 0.2	137	< 0.2	< 0.03	< 40	0.006	< 0.02	< 0.4	< 0.3	< 5
Animals													
Bison flesh	10.9	< 0.02	< 0.3	< 0.2	0.64	< 0.2	0.27	< 40	< 0.003	< 0.02	0.5	< 0.3	210
Mule deer flesh	8.6	< 0.02	< 0.3	0.9	0.65	< 0.2	0.16	< 40	< 0.003	< 0.02	0.5	< 0.3	178
Elk flesh	13.4	< 0.02	< 0.3	0.2	0.17	< 0.2	0.09	< 40	0.003	< 0.02	0.5	< 0.3	112
Grizzly bear flesh	19.3	< 0.02	< 0.3	0.5	0.56	< 0.2	0.06	< 40	0.003	< 0.02	0.5	< 0.3	100
Grizzly bear flesh	17.7	< 0.02	< 0.3	0.6	0.44	< 0.2	0.09	< 40	0.004	< 0.02	0.5	< 0.3	144
Grizzly bear hair	0.67	< 0.02	0.3	0.6	3.3	0.23	0.14	< 40	0.01	< 0.02	1.5	< 0.3	141
Grizzly bear hair	0.73	< 0.02	1.3	0.4	6.2	3.1	22.3	< 40	0.03	0.04	3.5	< 0.3	132
Grizzly bear hair	4.7	< 0.02	1.7	< 0.2	4.3	0.22	0.10	< 40	0.02	0.16	3.5	< 0.3	600
Grizzly bear hair	0.70	< 0.02	0.4	0.5	1.2	0.23	0.10	< 40	0.006	< 0.02	1.2	< 0.3	135

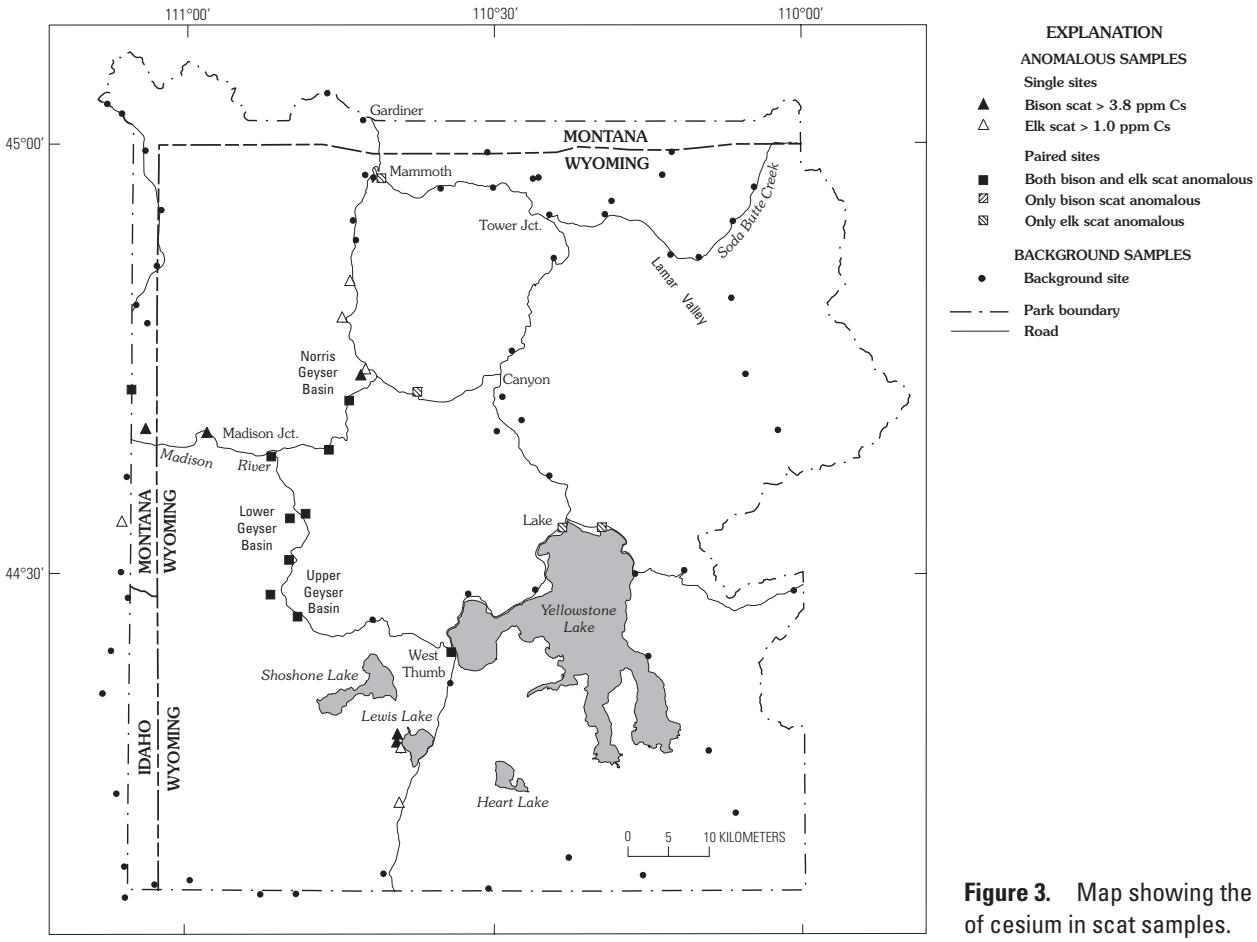

Figure 3. Map showing the distribution of cesium in scat samples.

plant-root masses. The relative distributions of this element in the two environments shown in table 6, as well as its classification into a separate factor by factor analysis, together indicate a relatively poor association of zinc with any particular lithology or with hydrothermal activity.

Figures 7 and 8 show the distributions of high and low concentrations (upper and lower quartiles) of percent ash in bison and elk scat, respectively. High values for both species (fig. 7) are generally concentrated in the Lamar River basin, the Mammoth-Gardiner area, and in the Upper and Lower Geyser Basins. In contrast, low ash values (fig. 8) are most common in samples collected around Yellowstone Lake (mostly bison) and in the southwestern part of the Park and vicinity (mostly elk). Although not plotted on any maps, both moose samples also showed a low percentage of ash (3.8 and 4.3 percent). The distributions of anomalously high or low percent ash for either bison or elk do not show any obvious strong spatial correlations to specific lithologies, or areas of past or present hydrothermal activity. The distribution of percent ash is probably related in part to the types of plants consumed at a given locality but mostly to the amount of soil mineral matter included in each sample.

Discussion

The scat of elk, bison, and moose that forage in thermal areas show enrichments in hydrothermal elements that are characteristically concentrated in thermal waters. These elements are enriched in the rocks altered by these waters and are also found in sinter and travertine deposits.

Fluorine is anomalous in rocks and sediments from many parts of the Park (Chaffee, Carlson, and King, this volume) and is strongly anomalous in geothermal waters (Miller and others, 1997). Anomalous fluorine has also been measured in forage plants growing in some hydrothermally altered areas in parts of the Park (J. Otton, oral commun., 2001; Garrott and others, 2002). Fluorine is the only element examined for this study that has been clearly documented to have a serious negative effect on Yellowstone wildlife (Garrott and others, 2002). This element, which is a necessary nutrient for animals at low concentration levels, has been recognized by biologists for some years as having a serious negative impact on the health and longevity of elk when ingested in large amounts (Shupe and others, 1984). We did not measure the fluorine content in elk-scat samples for this study. However, because it is one of the elements that is strongly associated with hydrothermal activity (Chaffee, Carlson, and King, this volume), one can infer that scat with

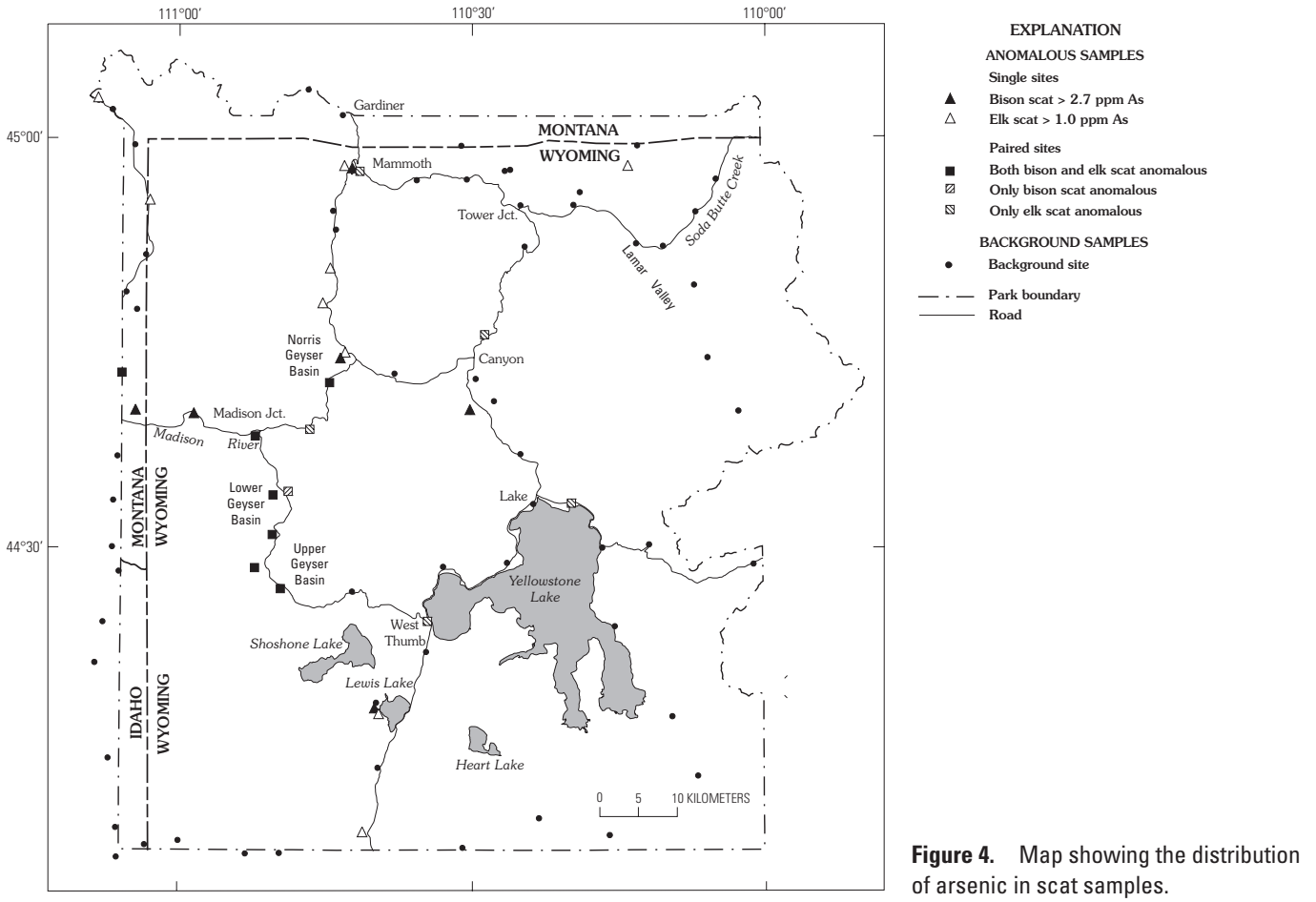

Figure 4. Map showing the distribution of arsenic in scat samples.

high concentrations of elements such as As, Cs, and Mo will probably also contain anomalous concentrations of fluorine.

Elements such as arsenic are also known to be concentrated in plant tissue and may be passed up the food chain to large animals. Some data on the arsenic content of plants are given in table 7. When compared to concentration levels in stream sediment collected in or near Yellowstone National Park, scat samples locally contain unusually high concentrations of the hydrothermally associated elements As, Br, Cs, Mo, Sb, and W, as well as of the vegetation-associated elements Ba, Ca, K, Rb, and Sr. Zinc, an element not related to any one rock type or to hydrothermal activity, is relatively enriched in scat as compared to sediment and is classified in a separate factor by factor analysis. The zinc data set also shows a distinct bimodal distribution. This overall unique behavior of zinc is not understood.

Several other elements that are known to be potentially toxic to wildlife (Cr, Hg, Ni, Pb, Se, and U) were also measured but were found to be present in only very low concentrations in scat. These low values reflect their generally low concentrations in rocks and stream sediments in the region (Chaffee, Carlson, and King, this volume) and in plants (table 7).

The spatial distributions of most of the element anomalies observed in scat for this report in general show no particular correlation with the underlying rock type. However, a spatial correlation between anomalous, hydrothermally related elements in scat and hydrothermally altered rocks does exist. Scat does not seem to be anomalous much more than about a kilometer or two beyond any of the altered areas. However, it may be anomalous downstream from some altered areas. Although most bison and elk in the Park move from place to place seasonally, some elk are nonmigratory in the geyser basins of the Madison River drainage basin. These observations, coupled with our chemical data, suggest that animals spending a considerable amount of time foraging in and near hydrothermal areas may eventually ingest significant amounts of one or more potentially toxic elements.

Additional hydrothermally related elements measured but not discussed in detail in this report include bromine and tungsten. These elements are distributed similarly to samples with anomalous concentrations of other hydrothermally related elements. The effects of ingestion by animals of bromine or tungsten, or any of the other hydrothermal elements discussed except fluorine, are uncertain. According to Puls (1988), a high fluorine uptake by cattle aggravates bromine toxicity. Tungsten in high concentrations is known to be toxic to plants and animals (Gough and others, 1979; Puls, 1988).

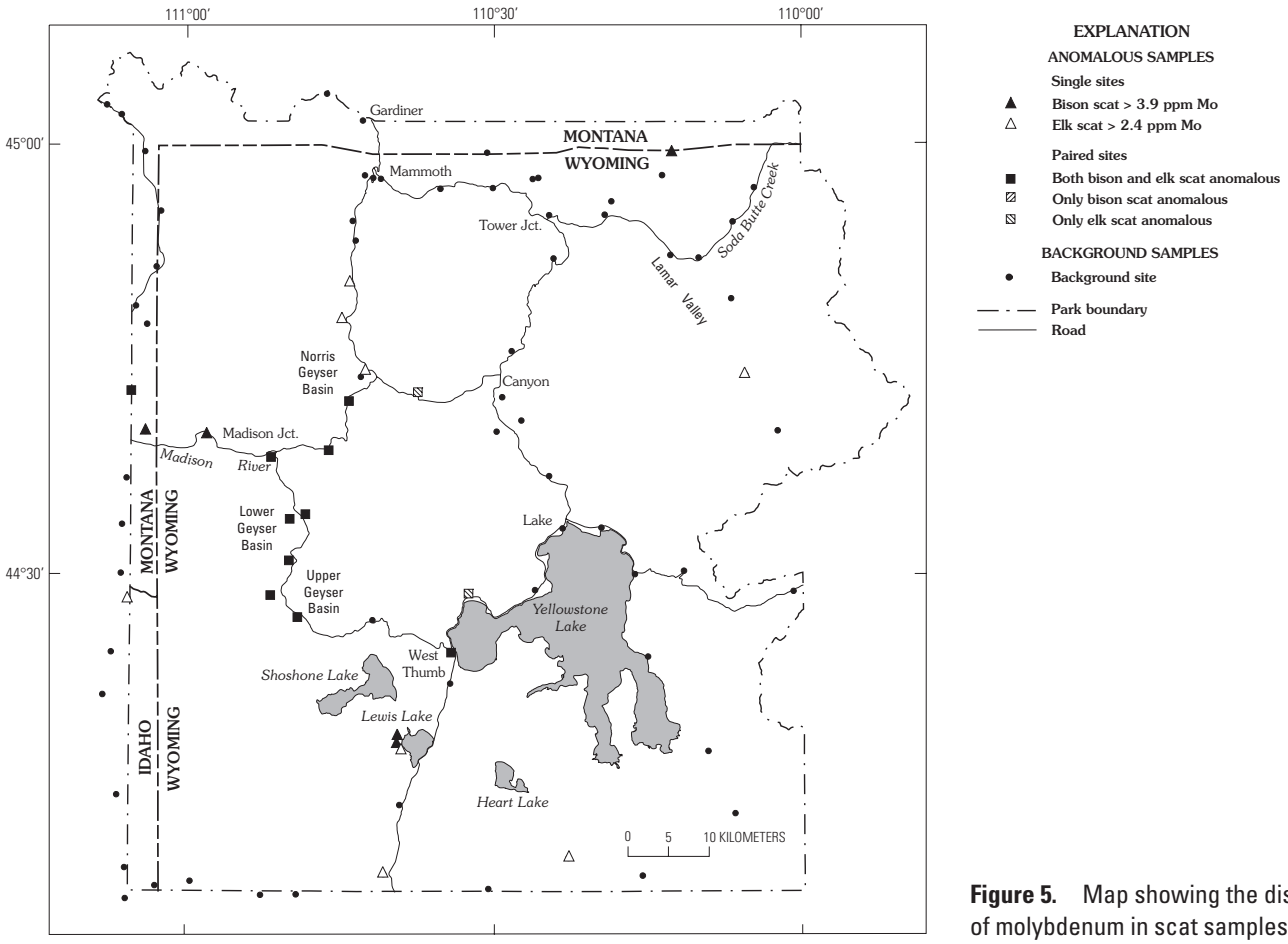

Figure 5. Map showing the distribution of molybdenum in scat samples.

Many plant species can be poisoned by the uptake of relatively large amounts of elements such as Ag, Al, As, B, Br, Cd, Cl, Co, Cr, Cu, F, I, Li, Mn, Mo, Ni, Pb, Tl, U, V, and Zn (Gough and others, 1979; Kabata-Pendias, 2001). This poisoning does not always kill the plants but may weaken them to the point that diseases become a threat. By analogy, this process may occur in animals in the Park but, with the exception of fluorine, may not be visually obvious. However, no obvious effects of bison ingesting toxic doses of any metals have been observed to date (Steve Sweeney, Univ. of Montana, written commun., 2002).

Ingestion of even relatively large amounts of a given element, whether from plants, soils, or water, probably does not demonstrate that the animals retain and accumulate the elements at any particular concentration level in their blood or tissues. Retention and toxicity of many elements depend on the chemical form of the element. Analyses of organs such as livers and kidneys, as well as hair, blood, and urine analysis, will be necessary to demonstrate retention and whether the levels found might be high enough to represent a health problem. Should high levels be found, they should be evaluated for any correlations (1) between high chemical levels in Park animals and incidence of diseases in these animals, and (2) to known areas within the Park having anomalous concentrations of the elements in question in rocks, soils, and (or) plants.

Impact of Sublacustrine Hydrothermal Elements on Cutthroat Trout and Grizzly Bears in the Yellowstone Lake Ecosystem

Yellowstone Lake is the last pristine habitat for the native Yellowstone cutthroat trout (*Oncorhynchus clarki bouvieri*), but the survival of this species is threatened as a result of the illegal or accidental introduction of the piscivorous lake trout (*Salvelinus namaycush*) into the lake. The presence of lake trout was discovered by an angler in 1994 (Kaeding and others, 1996). Since then, lake trout have had a serious, detrimental impact on the Yellowstone cutthroat trout population and have the potential to reduce the native cutthroat trout population by 80–90 percent (McIntyre, 1996).

This predation has led to an aggressive gill-netting program in Yellowstone Lake by the National Park Service to reduce the population of lake trout. Fishing regulations in Yellowstone Lake now allow unlimited catches of lake trout and require that any lake trout caught be killed, the stomach contents be examined, and the findings reported to Park rangers. Ruzycki and Beauchamp (1997) used data on angler-caught and gill-netted lake trout to produce a bioenergetics

model to estimate size-specific consumption of cutthroat trout by lake trout. They estimated that intermediate-size lake trout (301–499 mm long) consume 28 cutthroat trout per year and large lake trout (500–850 mm long) consume an average of 90 cutthroat per year.

The Yellowstone cutthroat trout are of critical importance to the Yellowstone ecosystem because they are an important prey food for grizzly bears, otters, eagles, and osprey. The potamodromous (migrate to and spawn in fresh-water streams) cutthroat trout are an especially important food source for grizzly bears (Mattson and Reinhart, 1995; Mealey, 1980; Reinhart, 1990), which have been designated as a threatened species. Bears feed on massive quantities of trout present in the tributaries to Yellowstone Lake during the spring cutthroat-spawning season. In contrast, the nonmigratory lake trout stay in deep water in the lake and spawn in the lake. Thus, lake trout are not accessible to grizzly bears and do not fill the same environmental niche as the Yellowstone cutthroat trout. Lake trout are also less accessible to otter, osprey, and eagles because of their tendency to stay in deeper water.

Balistrieri and others (this volume) have shown that Yellowstone Lake sublacustrine hydrothermal-vent waters contribute substantial amounts of As, B, Cl, Cs, Ge, Li, Mo, Sb, and W to the lake. Measurements of chloride concentrations in the lake indicate that about 10 percent of the total thermal-water flux in Yellowstone National Park occurs on the floor of Yellowstone Lake, mainly within the Yellowstone caldera, in the north part of the lake, and in the West Thumb area (fig. 1). In addition, Hg and Tl show substantial enrichment in vent fluids and in siliceous deposits near sublacustrine vents (Balistrieri and others, this volume; Shanks and others, this volume). Of these elements, As and Hg have a documented toxicity to wildlife, and Li, Mo, Sb, and Tl are potentially toxic elements (Smith and Huyck, 1999). The possibility that hydrothermal-metal fluxes affect the aquatic ecosystem, and possibly the greater Yellowstone ecosystem, follows from the discovery of three "cutthroat Jacuzzis" in Yellowstone Lake. These are shallow-water, low-temperature vents where schools of as many as 30 cutthroat trout congregate at a given time, presumably because of opportunities to feed on the bacteria and zooplankton that flourish in the nutrient-rich thermal waters.

For this study, metal concentrations in Yellowstone Lake fishes were determined, as were the sources and fates of these metals. Because spawning cutthroat trout are an important food source for the endangered grizzly bear, a special effort was made to measure potentially toxic elements in grizzly bear food sources and in bear tissues. The only previously published data on mercury in fish from Yellowstone National Park are from cutthroat trout sampled from the Yellowstone River, at the lake outlet, as part of the USGS Yellowstone River Basin NAWQA (National Water-Quality Assessment) Program

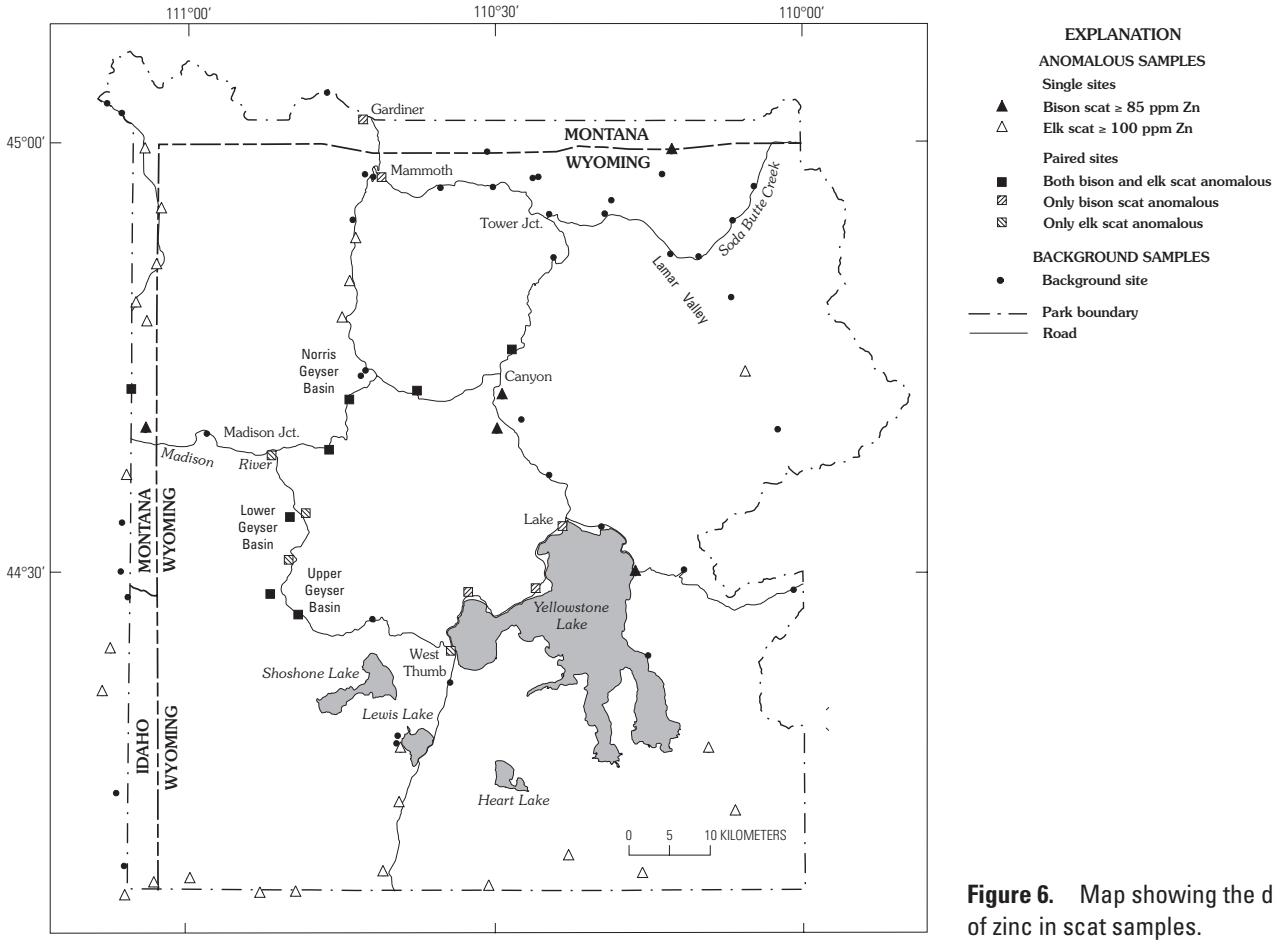

Figure 6. Map showing the distribution of zinc in scat samples.

(Peterson and Boughton, 2000). In that study, five cutthroat trout from this site were collected and their livers were analyzed for organic contaminants, potentially toxic metals, and other elements. Mercury concentrations in fish livers from this site averaged 0.54-ppm Hg (dry weight) and were enriched in comparison to most other fish-liver samples collected in the NAWQA study of the Yellowstone River drainage basin.

Collection, Preparation, and Analysis of Samples

For this study, lake and cutthroat trout were collected from Yellowstone Lake in 1998 and 2000, mostly by gill netting. Additional fish were caught in 1998 by line-fishing at near-shore sites, particularly in areas of known sublacustrine hydrothermal activity. Spawning cutthroat trout were also collected by the Interagency Grizzly Bear Study Team (IGBST). In all, 39 cutthroat trout and 25 lake trout were collected. Sample localities were chosen to give a broad geographical distribution in the lake, and included areas around West Thumb, Dot Island, Frank Island, Southeast Arm, South Arm, Sedge Bay, and Steamboat Point. Fish samples spanned a large range in size, from about 240–640 mm in length.

The 1998 samples were separated into stomach contents, muscle tissue, and liver tissue, which were analyzed separately. Analyses of fish collected in 2000 focused on muscle tissue. Following collection, all samples were frozen and stored in clean, sealed plastic bags until analysis. The 1998 samples were freeze-dried prior to analysis. Weight loss due to freeze-drying allowed calculation of water content, which averaged 76±7 weight percent. Fish collected in 2000 were analyzed directly without drying.

Samples of plants and animals consumed by bears, and of grizzly bear flesh and hair, were collected by the Interagency Grizzly Bear Study Team under direction of Chuck Schwarz, USGS-BRD. Samples selected were broadly representative of the foods grizzly bears are known to consume and were collected from widely separated localities in the Park, as described in the third section of this paper. Samples of bacterial and algal mats, and of plankton in the water column, were also collected from Yellowstone Lake, and subsamples for chemical studies were provided by J.V. Klump and R. Cuhel of the University of Wisconsin-Milwaukee.

All samples were chemically analyzed at the U.S. Geological Survey laboratories in Denver, Colo. The vegetation and tissue samples were first ground; the macerated material was then weighed (usually about 0.5 g) into a flint-glass test tube, 5 mL of concentrated Ultrex nitric acid was added, and the mixture was allowed to stand overnight. For the hair samples, the material was weighed and transferred to the test

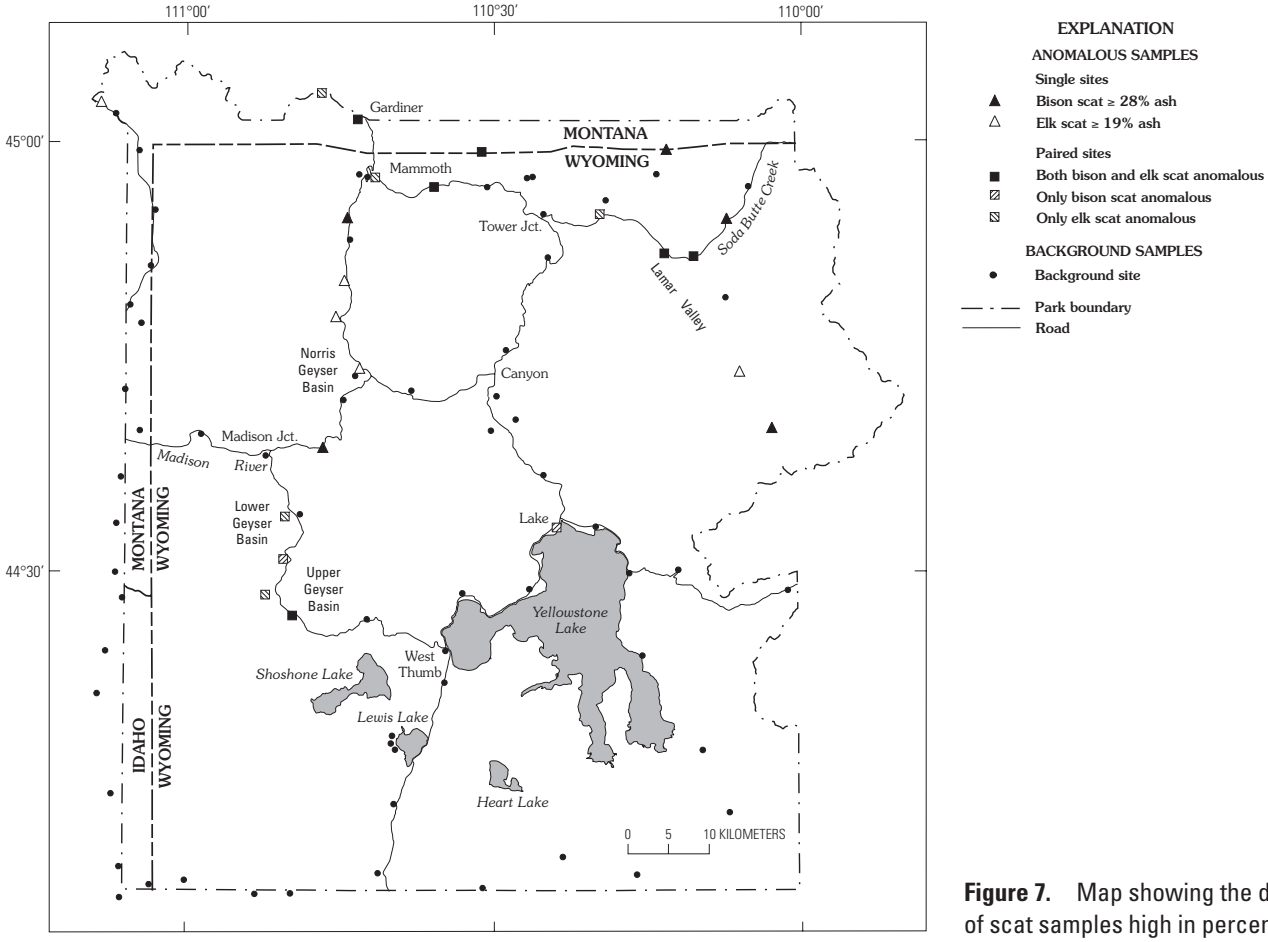

Figure 7. Map showing the distribution of scat samples high in percent ash.

tube. No attempt was made to macerate the material. The test tubes were heated in an aluminum block on a standard laboratory hot plate to about 95°C for about 2 hours. Three 1-mL aliquots of 30-percent hydrogen peroxide were added at 15-minute intervals to the hot digestate while still in the heating block. The resulting solution was heated for an additional hour at 95°C. The test tubes were removed from the hot plate, cooled, and the contents transferred to a new test tube. The volume was brought to a 20-mL volume in a clean test tube with nano-pure water. For the determination of mercury, a 5-mL aliquot of the sample digest was transferred to a clean test tube, 0.5 mL of a nitric acid–sodium dichromate solution was added, and the resulting mixture was brought to a 10-mL volume with nano-pure water. Mercury was determined using the continuous flow, cold-vapor, atomic-absorption spectrometer (CV-AAS) method. Blanks, duplicate samples (where sufficient material permitted), and standard reference materials from the National Institute of Standard Technology were included to insure data quality. The lower limit of determination is solution-based at about 0.1 ppm. Method error has been determined to be less than 5 percent RSD (relative standard deviation). Splits of the same samples were digested by heating in a nitric acid–hydrogen peroxide solution and analyzed for 39 elements by induction coupled plasma–mass spectrometry (ICP–MS) using a Perkin-Elmer model 6000 instrument (Lamothe and others, 1999).

Metal Concentrations in Trout

Concentrations of mercury and 39 other elements were determined in trout tissue and other types of samples (table 7). Mercury in cutthroat and lake trout muscle averaged 0.86 and 0.89 ppm on a dry-weight basis. This translates to an average of about 0.2 ppm on a wet-weight basis, and none of the muscle samples exceeded the 1.0-ppm (wet weight) Food and Drug Administration (FDA) action limit for human consumption (fig. 9). Thus, Yellowstone Lake fishes do not pose an immediate human-health risk, though some samples were close to the FDA's 1.0-ppm wet-weight limit for methyl mercury. Our samples were analyzed for total mercury, but there is good evidence that >95 percent of the Hg in fish tissue occurs as methyl mercury (Bloom, 1992). A comparison of the mercury concentrations in the Yellowstone trout to the mercury contents of marine fishes (from the FDA Web site: http://www.cfsan.fda.gov/~frf/sea-mehg.html) shows that both species of Yellowstone trout have mercury concentrations that are in the normal range, in contrast to species such as shark and swordfish that contain high concentrations of mercury (fig. 10).

Examination of the other metals analyzed (table 7) indicates that cutthroat and lake trout muscle, liver, and

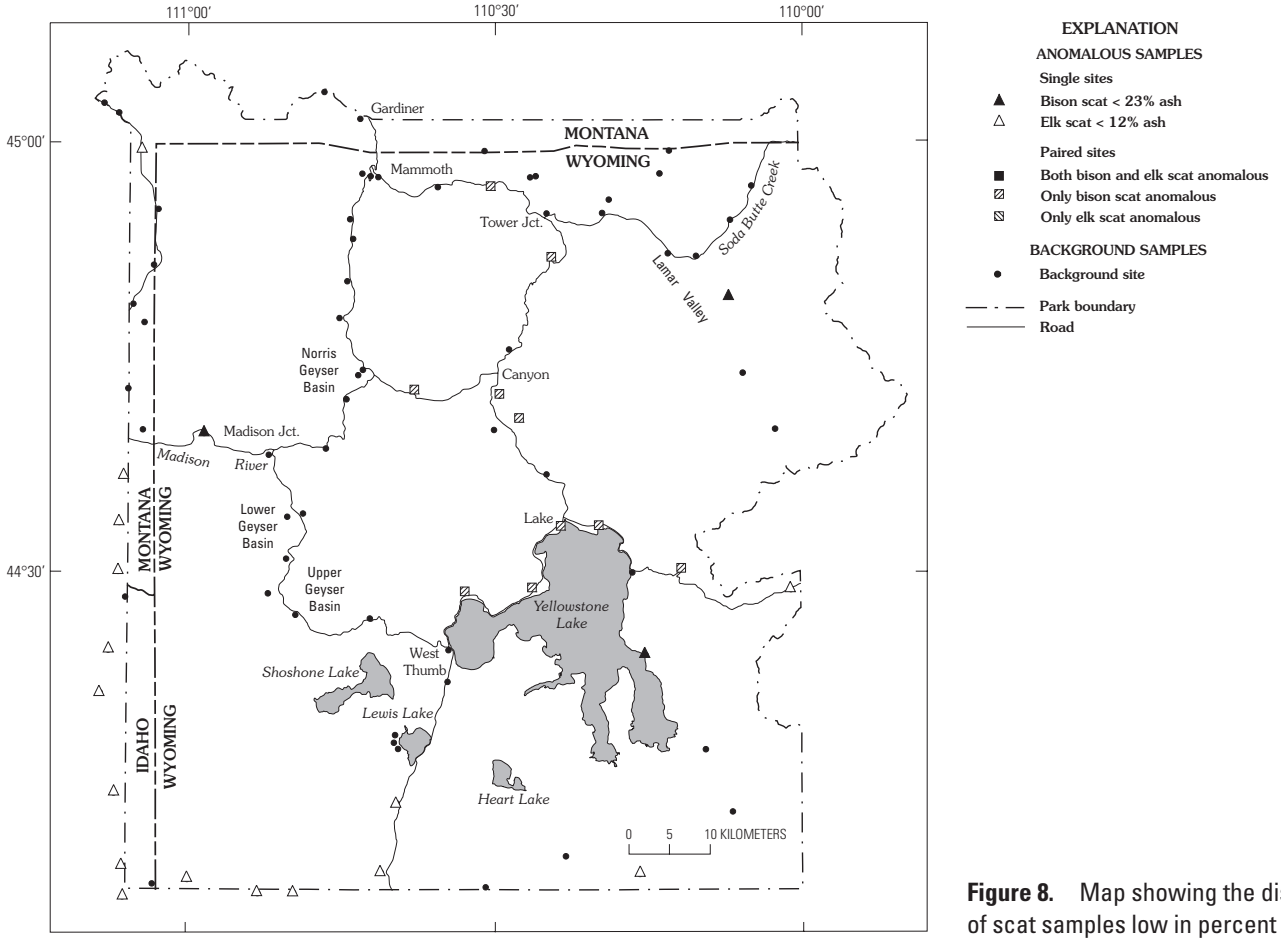

Figure 8. Map showing the distribution of scat samples low in percent ash.

stomach contents have relatively high concentrations of As, Hg, Se, and Tl. The average concentrations of arsenic in Yellowstone Lake fishes (cutthroat trout, 0.23 ppm, and lake trout, 1.4-ppm, dry weight, respectively, in muscle tissue) are well below FDA edible shellfish limits of 76–86-ppm wet weight (U.S. Food and Drug Administration, 2001). FDA limits have not been established for arsenic in fish or for selenium and thallium in seafood.

The average concentration of mercury in lake trout tissue from Yellowstone Lake is the same as that of cutthroat trout; thus, trophic enrichment is not apparent even though cutthroat trout are a major component of lake trout diet. Concentrations of selenium and thallium in muscle tissue show enrichments in lake trout relative to cutthroat trout of about the same factor (1.4). These enrichments may be evidence for trophic enrichment of selenium and thallium. Arsenic concentrations are higher in lake trout muscle than in cutthroat muscle, but many values are near the lower limit of analytical determination, so enrichment factors are probably not reliable for As in muscle. High concentrations of Cd, Cu, Mo, and Zn occur in liver and stomach contents of both cutthroat and lake trout, but these elements are not significantly enriched in the muscle. In addition, the concentration of arsenic in muscle is quite low compared to that in stomach contents, perhaps indicating that arsenic and these other elements are not readily accumulated in muscle tissue.

Sources of Metals

Hydrothermal-vent waters are a probable source of the metals found in the trout of Yellowstone Lake. Mercury ranges from <0.010 to 0.170 ppm in sublacustrine hydrothermal-vent fluids (Balistrieri and others, this volume). Bacterial and algal mats and plankton represent possible food sources for cutthroat trout, but the pathway of metals up the food chain is not known. Mercury must be methylated to be readily accumulated into animal tissue, and it is likely that methylation is caused by methanogenic or sulfate-reducing bacteria, possibly in thermally heated waters. Methylated mercury is also strongly accumulated in phytoplankton such as diatoms (Mason and others, 1995), which are very abundant in Yellowstone Lake. Methyl-mercury studies have not been carried out in the present investigation; only total mercury concentrations have been determined.

Our analyses of the stomach contents of cutthroat trout indicate that zooplankton, such as amphipods, which feed on phytoplankton or bacteria, are consumed by cutthroat trout. In the limited group of samples of bacteria, algae, phytoplankton, and macrophytes analyzed for this study, As, Mo, and Sb were detected in bacteria and plankton. Not enough sample material was available for mercury analysis. Antimony was also detected in the single macrophyte sample (table 7).

Analysis of the stomach contents of lake and cutthroat trout is perhaps the best measure of the metals they consume. All stomach contents were examined by binocular microscope, and several cutthroat trout showed a dominance of

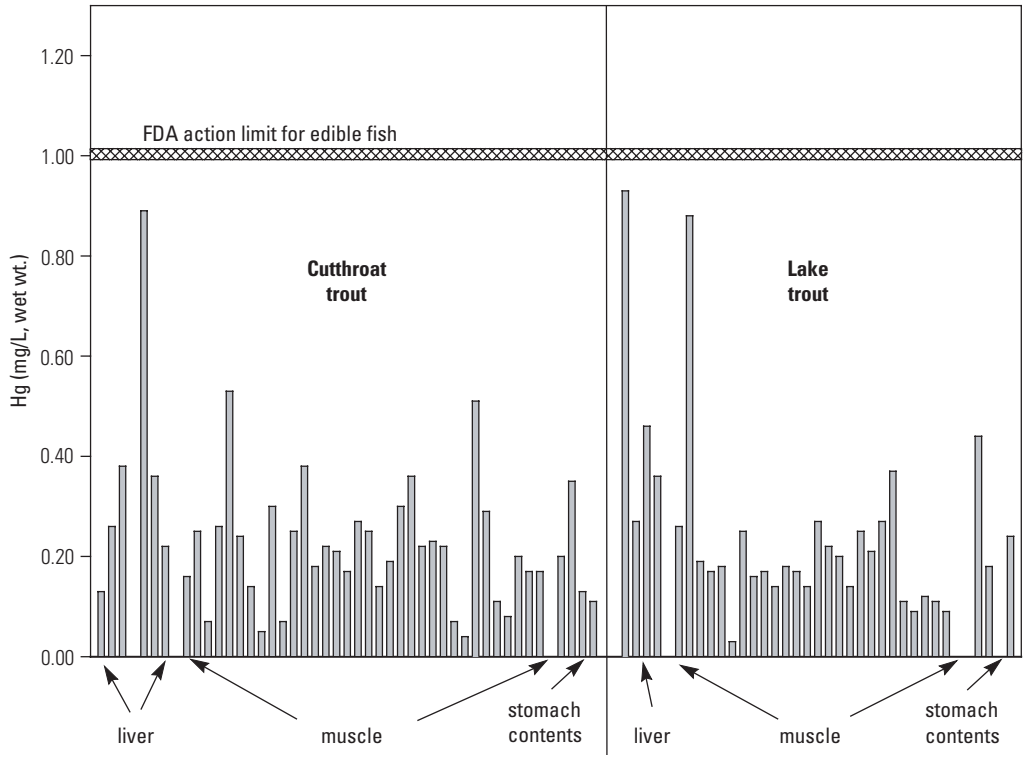

Figure 9. Mercury concentrations in cutthroat and lake trout.

amphipods. Amphipods have frequently been observed by a submersible camera in areas around sublacustrine vents in the lake and may be the principal food for cutthroat trout in vent areas. Arsenic, Cu, Hg, Mo, Se, and Tl are enriched in the stomach contents of both lake and cutthroat trout, whereas cadmium is enriched only in the stomach contents of lake trout (table 7).

The concentrations of As, Se, and Tl are higher in the stomach contents, livers, and muscles of lake trout than in the corresponding parts of cutthroat trout. Mercury is higher in the stomach contents and livers of lake trout than it is in the same parts of cutthroat trout, but it is present in similar concentrations in muscles from both species. For cutthroat trout, a weak correlation was observed between concentrations of mercury and fish size (fig. 11), but no such correlation seems to exist for lake trout. A possible explanation for this apparent lack of correlation in lake trout may be found in the studies of the otoliths (ear bones) of large lake trout from Yellowstone Lake (Ruzycki and Beauchamp, 1997). Some of the otoliths they studied may be from trout that are 20–21 years old. Microchemical studies of these otoliths show that the lake trout originated in Lewis Lake and were illegally introduced to Yellowstone Lake in late 1989 (Munro and others, 2001). Thus, as of this writing, the introduced lake trout have only been consuming mercury-bearing cutthroat trout for a part of their life cycle. Therefore, it is not surprising that trophic enrichment from cutthroat to lake trout is not indicated.

Stable isotope studies of C, N, and S (see study three, below) indicate that whitebark pine nuts and cutthroat trout are important foods for Yellowstone grizzly bears. However, pine nuts are not strongly enriched in any of the trace and minor elements studied (table 7, fig. 12). Other plants and animal flesh show some enrichment in Al, Ba, Mn, Rb, and Sr but not in the potentially toxic elements that are enriched in cutthroat trout. Notably, hair samples from grizzly bears are clearly enriched in mercury and are most strongly enriched in bears that live near Yellowstone Lake. Two hair samples collected near the lake have mercury concentrations of 0.61 ppm and 1.7 ppm (dry weight), respectively (table 7).

The sublacustrine hydrothermal activity in Yellowstone Lake provides a powerful tracer of the importance of fish consumption by grizzly bears. Mercury enrichment in the hair of bears living near Yellowstone Lake almost certainly documents their consumption of spawning cutthroats in early summer. This ability to trace fish consumption through mercury levels in hair is important because it offers a tool to determine how much of the bear population currently consumes fish and how far individual bears may travel to the spawning tributaries of Yellowstone Lake to eat these fish. This information is potentially important to wildlife managers who need to evaluate the ability of the bear population to adjust to possible decrease in cutthroat trout populations due to predation by lake trout.

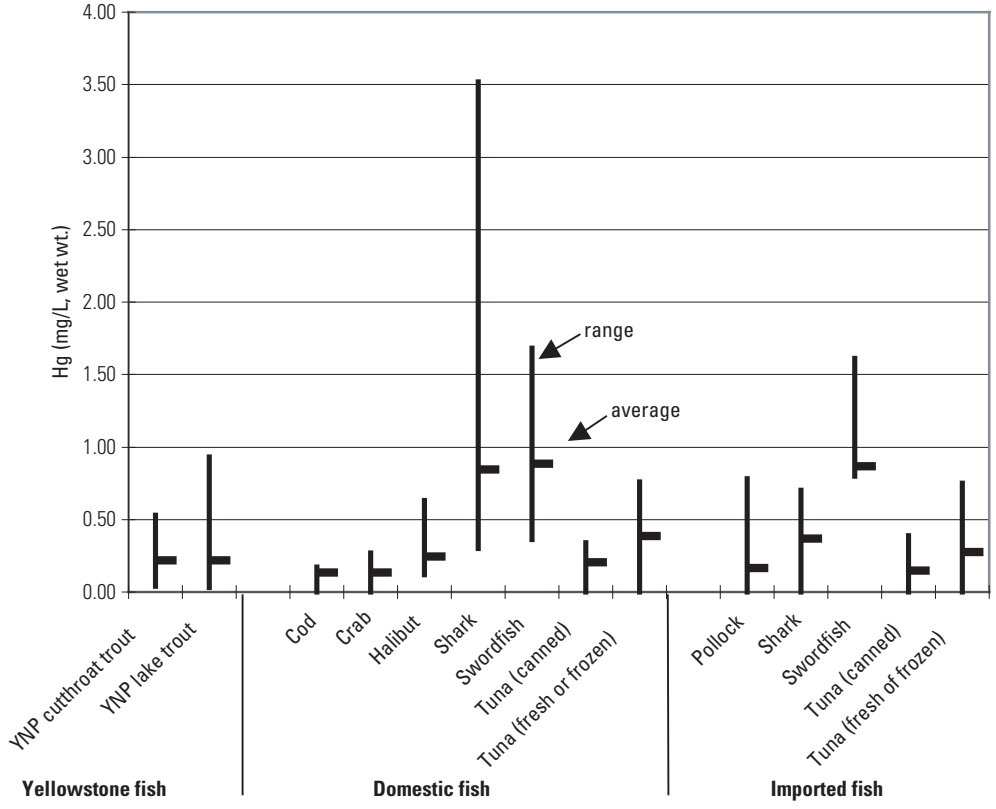

Figure 10. Mercury concentrations in common species of domestic and imported fish.

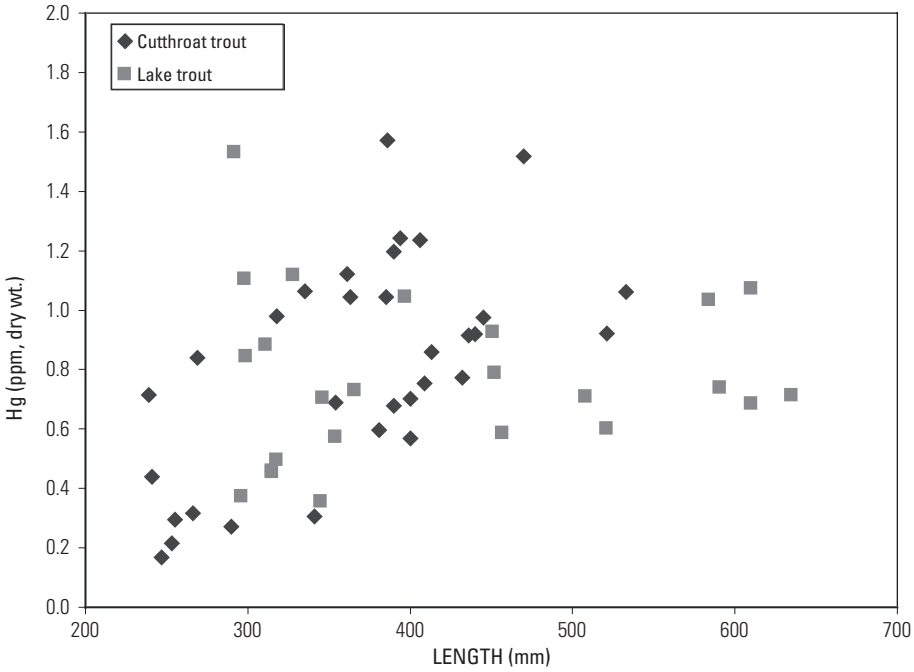

Figure 11. Mercury concentrations in muscle tissue of cutthroat and lake trout.

Carbon-, Nitrogen-, and Sulfur-Isotope Studies of Grizzly Bears (*Ursus arctos*) and Their Foods in the Yellowstone Ecosystem

Beginning in the 1950s with the first isotopic analyses of thermal waters (Craig and others, 1956), stable isotopes have played an important role in understanding the geochemical evolution of the thermal areas and igneous rocks of Yellowstone (see papers in this volume and those referenced in Bargar and Dzurisin, 1986). Recently, stable-isotope studies have been increasingly applied to investigations of ecosystems (Hobson and Wassenaar, 1999; Peterson and Fry, 1987). Stable-isotope applications to diet and food-web studies began with work by DeNiro and Epstein (1981), who showed that carbon- and nitrogen-isotope ($\delta^{13}C$ and $\delta^{15}N$) compositions in animal tissue reflect those of their diet. Fractionation of these isotopes can occur via metabolism and protein synthesis. This fractionation results in higher ratios in consumers relative to their prey; animal tissue is enriched in ^{13}C relative to diet by about 1 ‰ and in ^{15}N by about 3 ‰ (DeNiro and Epstein, 1978, 1981; Fry and Scherr, 1984; Minagawa and Wada, 1984). Sulfur-isotope ($\delta^{34}S$) compositions generally show a small depletion (1–2 ‰) in ^{34}S or no shift in values between consumers and diet (Kester and others, 2001; Krouse, 1989; Neill and Cornwell, 1992; Peterson and Fry, 1987).

This study describes the preliminary results of a stable-isotope study of grizzly bears (*Ursus arctos*) in a part of the greater Yellowstone ecosystem (Schwartz and others, 2002). The purpose of this investigation is to determine the extent to which stable isotopes, particularly those of sulfur in conjunction with carbon and nitrogen, can be used as (1) tracers of nutrient (C, N, and S) sources and processes that occur in the transfer of nutrients, beginning with the elements in rocks and waters and continuing through the rest of the grizzly bear food chain, and (2) aids to understanding the ecology and demographics of grizzly bears. The second aspect of this study is important because some food sources of grizzly bears in the Yellowstone ecosystem may decline, and wildlife managers must understand how the dynamics of this bear population might change in relation to changes in food abundance and distribution.

Grizzly Bear Food Sources

The Interagency Grizzly Bear Study Team (IGBST) was created in 1973 to monitor long-term population status and habitats of Yellowstone grizzly bears. A major goal of the 1993 grizzly bear recovery plan is to provide a scientific basis for the protection of grizzly bear habitat by conducting research on habitat use and food habits. The scientists of the IGBST have identified four major food components in the grizzly bear diet (Mattson and others, 1991). These include whitebark pine (*Pinus albicaulis*) nuts, a significant fall food that is rich in fat (Lanner and Gilbert, 1994); meat from bison (*Bison bison*) and elk (*Cervus elaphus*), which is a significant source of both digestible protein and energy; meat from cutthroat trout (*Oncorchynchus clarki*), also rich in protein; and cutworm moths (*Euxoa auxilaris*), which are high in fat. The abundance of these foods varies both seasonally and annually. For example, the amount of meat from ungulates depends largely on the availability of winter kill, particularly for bison. Bears also consume a wide variety of grasses, sedges, and forbs, as well as other animal matter, such as ants. As discussed below, at least two of the four major food sources in Yellowstone may decline in the

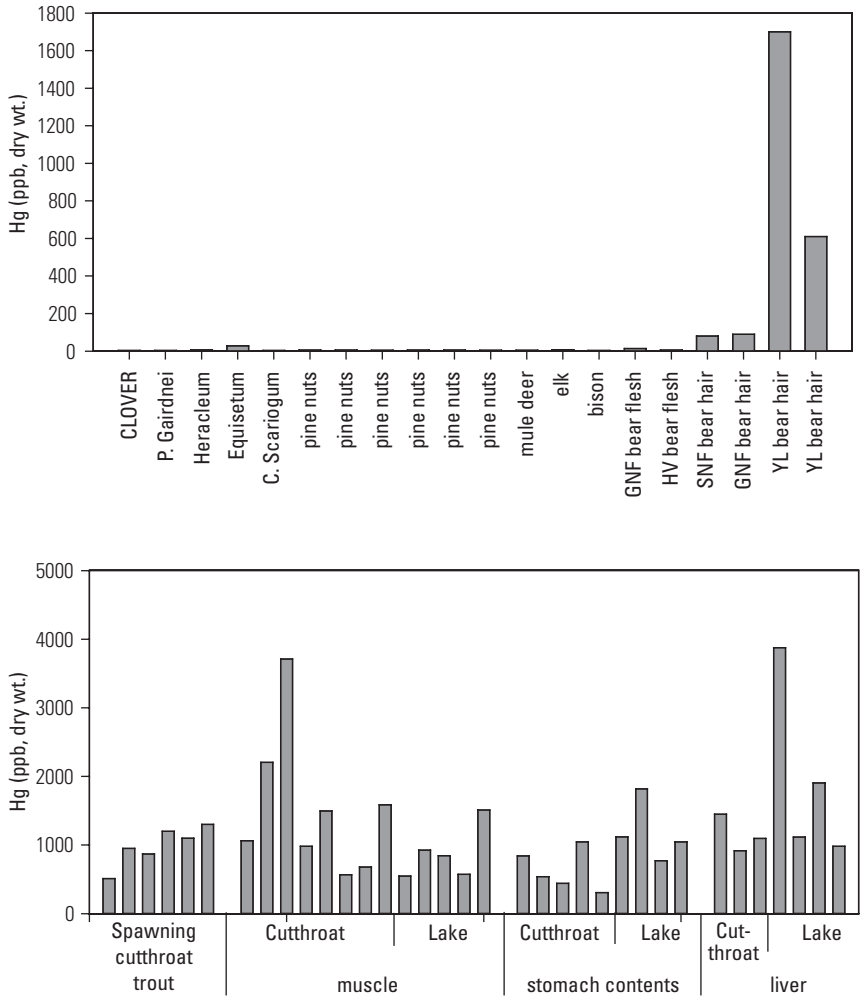

Figure 12. Mercury concentrations in plants and animals in greater Yellowstone ecosystem. GNF, Gallatin National Forest; HV, Hayden Valley; SNF, Shoshone National Forest; YL, Yellowstone Lake.

future. Thus, the need to understand the relationships between the population demographics of grizzly bears and their major food resources is important. Traditionally this type of information has been obtained through long-term telemetry studies, scat analysis, and observations. Stable-isotope studies of hair may offer a cost-effective method to quantify how the grizzly bear population utilizes food resources.

Grizzly bear consumption of spawning cutthroat trout found in tributaries of Yellowstone Lake has been well documented (Mattson and Reinhart, 1995; Mealey, 1980; Reinhart, 1990). The army cutworm moth is also an important, although unquantified, caloric contribution for about one-third of the grizzly bears in the Yellowstone ecosystem (White, 1996; White and others, 1999). The IGBST has identified more than 40 moth sites where grizzly bears feed, primarily in Shoshone National Forest, just to the east of Yellowstone National Park. This moth is an agricultural pest affecting alfalfa and wheat crops on the Great Plains.

Whitebark pine, a masting species, produces significant cone crops at irregular intervals. Cone production varies from as many as 50 per tree to as few as two (Haroldson, 2000). Consumption of pine nuts is considerable in years of abundant crops. Grizzly bear mortality is 1.8–3.3 times greater in years of poor nut crops (Mattson, 1998). Female grizzly bears, especially, tend to feed on pine nuts, a food which may be critical to their reproductive success (Mattson, 2000). Whitebark pine in the Yellowstone ecosystem is infected with an exotic fungus (*Cronartium ribicola*), commonly known as white pine blister rust (Kendall and Keane, 2000). In the Western United States and Canada, 50–100 percent of the extant whitebark pine trees are either dead or dying. Recent surveys (Kendall and Keane, 2000) suggest that this fungus is spreading.

Collection, Preparation, and Analysis of Samples

Samples were collected from a number of widespread localities in the Yellowstone ecosystem (table 8). However, no attempt was made to conduct detailed, systematic sampling. Samples of grizzly bear hair were collected at various sites in the greater Yellowstone ecosystem as part of an ongoing DNA study (Haroldson and Podruzny, 2001). The DNA analyses require only the follicles, so the remainder of each hair sample was

available for stable-isotope and trace-element studies. Theoretically, grizzly bear hair can contain a sequential record of diet. However, growth rates of grizzly bear hair may not be uniform. Samples of hair that are collected from hair corrals for DNA studies are typically samples from hair grown the previous year.

Freeze-dried samples of muscle tissue from two bear carcasses, as well as tissue from elk, bison, and deer road-kill, were also obtained. Vegetation, including clover (*Trifolium* sp.), cow parsnip (*Heracleum* sp.), and spring beauty (*Claytonia* sp.), were collected during the growing season and air dried. Cutthroat and lake trout were collected from Yellowstone Lake using gill nets, and portions of filets were freeze-dried. Spawning cutthroat trout were also collected from a tributary to Yellowstone Lake. Additionally, moths were collected from six sites located throughout the ecosystem, including five lowland agricultural sites east of the Park boundary; these were also freeze-dried. Whitebark pine nuts were collected from several sites in the greater Yellowstone ecosystem and analyzed without further treatment.

Samples were analyzed for carbon- and nitrogen-isotope compositions by continuous-flow methods described by Fry and others (1992) on a Micromass Optima mass spectrometer. Samples were analyzed for sulfur-isotope compositions by continuous-flow methods described by Kester and others (2001) on a Finnigan Delta Plus XL. Hair and meat-tissue samples were analyzed for sulfur directly. Vegetation, moth, and nut samples were first treated with Eschka's mixture to extract sulfur, as described in Kester and others (2001). Results are reported as ratios relative to Peedee limestone ($\delta^{13}C$), atmospheric nitrogen ($\delta^{15}N$), or Canyon Diablo troilite ($\delta^{34}S$) as follows:

$$X = \{[R_{sample}/R_{standard}] - 1\} \times 10^3$$

where X is $\delta^{13}C$, $\delta^{15}N$, or $\delta^{34}S$ and R is $^{13}C/^{12}C$, $^{15}N/^{14}N$, or $^{34}S/^{32}S$. Units are in the per mil (‰) notation, which indicates 0.1 percent deviation from the standard per unit.

Results

The $\delta^{13}C$ values in the Yellowstone ecosystem range from –21.7 ‰ to –30.4 ‰; $\delta^{15}N$ values range from about 1 ‰ in plants to 11 ‰ in lake trout and almost 9 ‰ in bears; $\delta^{34}S$ values for vegetation range from about 3 ‰ for plants to more than 11 ‰ for pine nuts. The $\delta^{34}S$ values for animal tissue range from about –3 ‰ to 9 ‰, with the largest values recorded for bears (table 8). Spawning cutthroat trout show nearly 2 ‰ enrichments in ^{34}S but show no significant corresponding enrichments in ^{13}C or ^{15}N.

Both cutthroat and lake trout from Yellowstone Lake show large but different $\delta^{15}N$ values and similar $\delta^{13}C$ values (fig. 13). Moths show a wide range of $\delta^{15}N$ values and a narrow range of $\delta^{13}C$ values. The values for vegetation (clover and spring beauty), moths, ungulates, and bear tissue (hair and muscle) fall on a trophic-enrichment trend for bear food sources (fig. 13) (Hilderbrand, and others, 1996). The bears and their food sources show distinct $\delta^{15}N/\delta^{34}S$ (fig. 14) and $\delta^{13}C/\delta^{34}S$ (fig. 15) values. In particular, whitebark pine nuts have a distinct $\delta^{15}N/\delta^{34}S$ signature when compared to other bear foods (fig. 14), suggesting that consumption of nuts may be distinguishable by the isotopic signatures of bear tissue. The plot of $\delta^{13}C$ against $\delta^{34}S$ (fig. 15) also suggests that values are relatively invariant across animal food sources but that values for nuts are significantly different from those of other vegetable food sources.

Discussion

Carbon-Isotope Variations in the Food Chain

Carbon isotopes can be used to distinguish between the photosynthetic pathways of C_3 versus C_4 plants (Cerling and Quade, 1993). Stable-carbon-isotope ratios of C_3 plants can range from –20 ‰ to –35 ‰ and C_4 plants can range from –7 ‰ to –15 ‰ (Ehleringer, 1989). The $\delta^{13}C$ values of the grizzly bears, moths, and other animal tissues range from about –26 ‰ to –21 ‰ and are constrained by the –30 ‰ to –22 ‰ values for plants and pine nuts (fig. 13). The $\delta^{13}C$ values for the vegetation are consistent with an organic-carbon reservoir that is dominated by C_3 plants and also show slight trophic enrichments through the food chain. Grizzly bear eating habits also agree with this trend in that the grass component of the diet is in the C_3 category. The difference in $\delta^{13}C$ values in the plants versus the nuts may in part reflect the effect of elevation on the $\delta^{13}C$ values (Körner and others, 1991). Differences in $\delta^{13}C$ values between those of low-elevation plants and those of high-elevation whitebark pine nut samples may be related to the isotope effects associated with the availability of pore water in soils. $\delta^{13}C$ values are higher in dry, upland sites as compared to lower and wetter sites (Angradi, 1994; Ehleringer and Cooper, 1988). Bear hair is slightly more enriched in ^{13}C than is muscle tissue, a fact consistent with physiological differences in carbon-isotope fractionation processes between hair and muscle tissue (Hilderbrand and others, 1996).

Nitrogen-Isotope Trophic Enrichment in the Grizzly Bear Food Chain

Lowland-vegetation and whitebark pine nut $\delta^{15}N$ values (~0 ‰), are similar to atmospheric nitrogen and reflect values for nitrogen from nitrate or ammonia in soil waters, which come mainly from the decomposition of organic material in soils. Comprehensive data for all components of the aquatic ecosystem in Yellowstone Lake do not exist. However, the relatively high $\delta^{15}N$ values for fish from the lake suggest that the aquatic ecosystem acquires nitrogen from a ^{15}N-enriched source, possibly one associated with hydrothermal activity in the lake. Grizzly bears and most of their food sources (fig. 13) show a classical trophic-enrichment pattern as determined from a study of captive and wild bears (Hilderbrand and others, 1996). $\delta^{15}N$ values increase, in order, from plants and nuts to ungulates to bears. Interestingly, the $\delta^{15}N$ values for both cutthroat and lake

Table 8. Summary of stable-isotope data on grizzly bear tissue and their food sources showing average values, standard deviation, and number of analyses.

Sample	Location	Tissue	$\delta^{13}C_{PDB}$		$\delta^{15}N_{AIR}$		$\delta^{34}S_{CDT}$	
			average	1 σ (n)	average	1 σ (n)	average	1 σ (n)
Plants								
Clover *(Trifolium sp.)*	Yellowstone National Park (YNP)	plant	-28.4	0.54 (3)	-1.2	0.6 (2)	3.2	0 (2)
Cow Parsnip (*Heracleum sp.)*	YNP	plant	-28.4	(1)			2.7	(1)
Spring Beauty (*Claytonia sp.)*	Bridger-Teton National Forest	plant	-30.4	0.1 (2)	-1.5	0.0 (2)		
White Bark pine nuts								
(Pinus albicaulis)	Gallatin National Forest	nut	-24.5	0.6 (4)	-2.3	0.1 (3)	11.4	(1)
(Pinus albicaulis)	Gallatin National Forest	nut	-21.7	0.6 (2)	-1.7	0.5 (2)		
(Pinus albicaulis)	Shoshone National Forest	nut	-24.4	0.9 (4)	0.2	0.3 (3)	8.8	0.4 (2)
(Pinus albicaulis)	Custer National Forest	nut	-25.3	0.7 (3)	-1.8	0.0 (2)	9.2	(1)
(Pinus albicaulis)	Beaverhead National Forest	nut	-23.6	0.9 (4)	-0.5	0.6 (2)	8.3	(1)
(Pinus albicaulis)	Targhee National Forest	nut	-24.6	0.8 (7)	-1.0	0.4 (3)	8.5	(1)
Moths								
(Euxoa auxilaris)	Venus	body/wing	-26.2	0.5 (3)	8.0	2.3 (3)		
(Euxoa auxilaris)	Colter Basin	body/wing	-26.3	0.1 (3)	5.5	1.5 (3)		
(Euxoa auxilaris)	Ptarmigan/Clocktower	body/wing	-26.3	0.7 (4)	6.2	1.3 (4)		
(Euxoa auxilaris)	Sunlight	body/wing	-26.0	0.4 (5)	6.8	2.6 (5)		
(Euxoa auxilaris)	Carter Mtn.	body/wing	-26.4	0.7 (22)	6.6	2.1 (21)	-0.1	0.3 (3)
(Euxoa auxilaris)	5 sites in Wyoming	body/wing	-26.2	0.7 (15)	4.1	2.3 (15)	3.9	(1)
Ungulates								
Mule deer (Odocoileus hemionus)	YNP	flesh	-25.1	(1)	4.9	(1)	-3.1	(1)
Elk (Cervus elaphus)	YNP	flesh	-24.7	(1)	3.6	(1)	0.9	(1)
Bison (Bison bison)	YNP	flesh	-23.4	(1)	5.8	(1)	1.7	(1)
Lake trout								
(Alvelinus namaycush)	West Thumb, Yellowstone Lake	filet	-24.6	1.0 (5)	11.0	0.4 (5)	1.0	0.5 (5)
Cutthroat trout								
(Oncorchynchus clark)	West Thumb, Yellowstone Lake	filet	-22.5	1.3 (7)	8.3	1.0 (7)	1.4	0.2 (7)
Spawning cutthroat trout	Clear Creek, YNP	filet	-22.3	2.1 (6)	7.5	0.5 (6)	3.3	0.3 (3)
Grizzly bears								
(Ursus arctos horribilis)	Gallatin National Forest	flesh	-23.0	(1)	8.4	(1)	5.4	(1)
(Ursus arctos horribilis)	Gallatin National Forest	hair	-22.5	(1)	7.1	(1)	8.7	(1)
(Ursus arctos horribilis)	Hayden Valley, YNP	flesh	-23.6	(1)	8.8	(1)	3.2	(1)
(Ursus arctos horribilis)	Yellowstone Lake, YNP	hair	-21.9	0.1 (2)	7.0	1.5 (2)	6.5	0.1 (2)
(Ursus arctos horribilis)	Shoshone National Forest	hair	-21.8	(1)	6.7	(1)	6.1	(1)

trout are equal to, or greater than, the values for grizzly bears. As expected, the $\delta^{15}N$ values for lake trout are larger than the corresponding values for the cutthroat trout on which they routinely feed. The anomalously large $\delta^{15}N$ values for the fish in Yellowstone Lake need to be studied further. However, these values are believed to be related to the fact that the cutthroat trout feed on crustaceans (amphipods) that in turn feed on bacteria that grow around sublacustrine thermal vents. The $\delta^{15}N$ value of the contents (largely amphipods) of a cutthroat stomach was determined to be 5.6 ‰, consistent with this possibility. The fact that the $\delta^{15}N$ values in bears are not larger than those in cutthroat trout reflects the fact that bears are omnivorous, whereas trout are carnivorous. Although some bears eat cutthroat trout during the spawning season, average $\delta^{15}N$ values of hair indicate a significant vegetation-related component to bear diets. Our analyses were of hair that had completed its growth during the previous year. This hair contains an isotopic record of all foods consumed by the bear during the previous year's active (nondenning) season. Because bears only consume cutthroat trout for a short period of time during the spawning season in the spring and early summer, and because a significant portion of their diet the rest of the year is vegetable matter, the $\delta^{15}N$ value of total hair samples cannot be equal to or greater than that of trout. The same argument is valid for bear muscle tissue.

As discussed earlier, cutthroat trout tissues have high mercury concentrations, and high mercury concentrations in bear hair can be used as a tracer of cutthroat consumption. The samples of bear hair do not show large $\delta^{15}N$ values typical of fish consumption because the bears probably grew most of their hair in the fall when they were not eating fish. This interpretation is supported by the fact that the samples of bear hair have large $\delta^{34}S$ values that are consistent with the consumption of ^{34}S-enriched nuts in the fall.

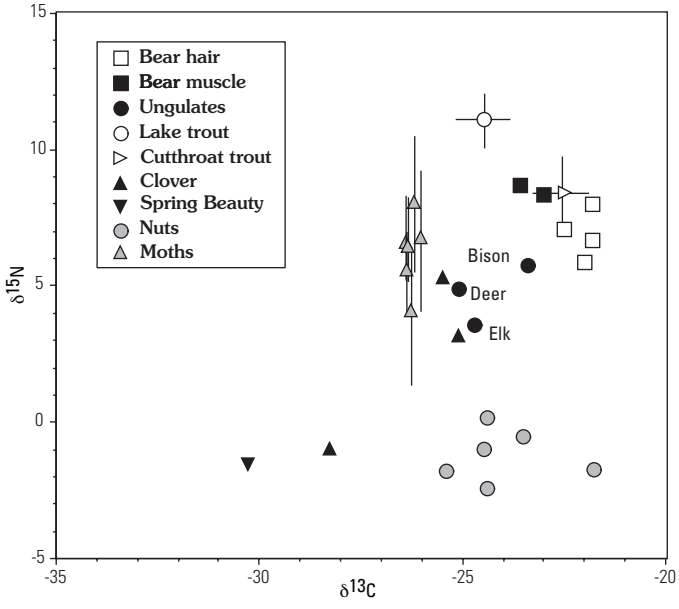

Figure 13. $\delta^{15}N$ and $\delta^{13}C$ values for bear tissue, bear food sources, and lake trout.

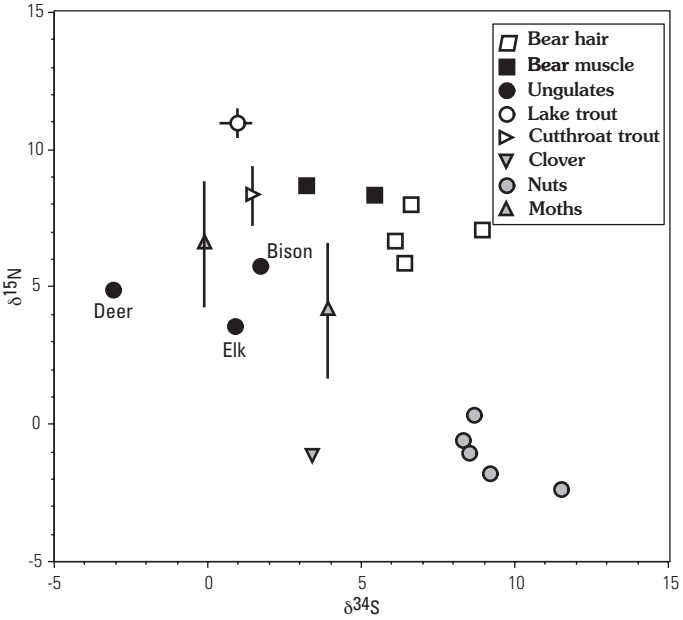

Figure 14. $\delta^{15}N$ and $\delta^{34}S$ values for bear tissue, bear food sources, and lake trout.

Sulfur-Isotope Variations in Grizzly Bears and Their Food Sources

The $\delta^{34}S$ values of grizzly bears (both muscle and hair) are larger than all of their meat food sources. The $\delta^{34}S$ values of whitebark pine nuts are larger than all the other vegetation sources that we measured, which indicates that the pine trees may assimilate sulfur from a different source, an observation consistent with studies of sulfur isotopes in trees from other locations (Krouse, 1980). The range of $\delta^{34}S$ values for grizzly bears and whitebark pine nuts indicates that bears are probably consuming the whitebark pine nuts, an isotopically heavy source of S, during hair growth. Clearly more work is needed on the fractionation of sulfur isotopes in grizzly bears (and food sources) such as described by Hilderbrand and others (1996). If sulfur-isotope fractionations related to physiological processes are not large, as indicated by Kester and others (2001), Krouse (1989), and Peterson and Fry (1987), our sulfur-isotope data are consistent with the possibility that whitebark pine nuts are a substantial component of the diet for some bears during hair growth.

Stable-Isotope Data as Tracers of Geologic and Environmental Sources and Processes in Ecosystems

Detailed sulfur-isotope studies of rocks at Yellowstone have not been made. However, general sulfur-isotope variations can be inferred from sulfur-isotope data from the thermal areas at Yellowstone (Schoen and Rye, 1970). $\delta^{34}S$ values in H_2S from thermal springs, and in sulfate produced from the oxidation of H_2S, range from –5.5 ‰ to 2.3 ‰. The lowest values are found in areas outside of the Yellowstone caldera margin (fig. 1), where thermal waters interact with sedimen-

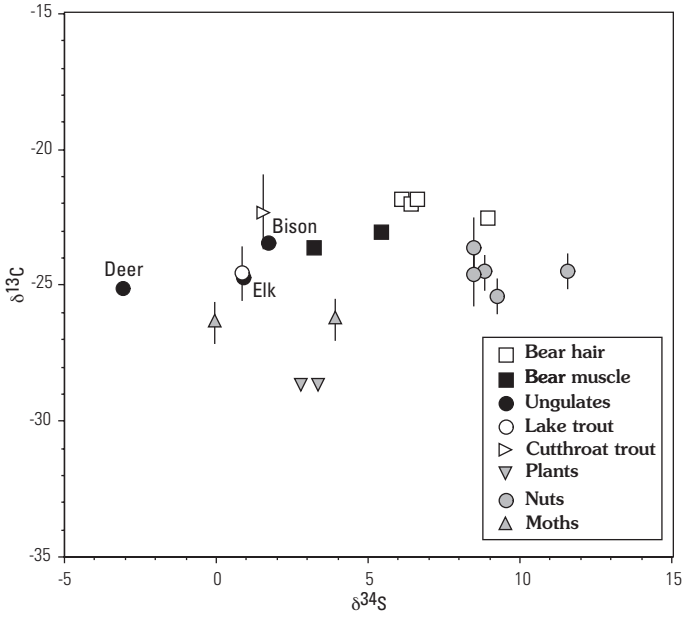

Figure 15. $\delta^{13}C$ and $\delta^{34}S$ values for bear tissue, bear food sources, and lake trout.

tary rocks at depth. The large flux of H_2S to the atmosphere from the thermal areas affects the $\delta^{34}S$ of sulfate in rain and snow in the Yellowstone area (Mast and others, 2001). The weighted-average-$\delta^{34}S$ value for sulfur in the thermal areas, which provide a representative value for the rhyolitic volcanic rocks that underlie much of the Park, is approximately 2±1 ‰. The average $\delta^{34}S$ value for much less abundant sulfate in these igneous rocks can be inferred from the sulfur-isotope fractionations between sulfide and sulfate phases observed in numerous studies of similar igneous rocks (Ueda and Sakai, 1984). This average $\delta^{34}S$ value for sulfate is inferred to be about 8±1 ‰ (Ueda and Sakai, 1984). The $\delta^{34}S$ values of sedimentary sulfide can vary widely but are normally less than 0 ‰ (Ohmoto and Goldhaber, 1997). That this is the case at Yellowstone is indicated by the low $\delta^{34}S$ values for H_2S from thermal areas on the margins of the caldera, where deep fluids interact with sedimentary rocks (Schoen and Rye, 1970). The $\delta^{34}S$ values for sedimentary sulfate depend on the age of the rocks and, in the case of the Mississippian Madison Group in the Yellowstone area, are probably close to 15 ‰ (Holser and Kaplan, 1966). Further work must be done to determine the $\delta^{34}S$ for sulfate and sulfide in volcanic and sedimentary rocks of the Yellowstone area, as well as to calibrate enrichment factors for sulfur isotopes in the Yellowstone food chain. It is encouraging, however, that the $\delta^{34}S$ values determined for the biological samples are bracketed by inferred values for sulfur sources in the igneous and sedimentary rocks, respectively, in the Yellowstone area. Thus, it appears that $\delta^{34}S$ values can be used to trace organic sulfur within the food chain from its origin in specific geologic sources to various flora and fauna.

Nitrogen-isotope values in the Yellowstone ecosystem generally follow trophic-enrichment patterns; however, both species of trout have high $\delta^{15}N$ values relative to those of bears. The large $\delta^{15}N$ values in trout provide a tracer for environmental nitrogen that is related to hot-spring activity in Yellowstone Lake (Estep and Macko, 1984).

Our preliminary study indicates that isotope data (especially when combined with trace-element data) offers an excellent method to trace bear-feeding ecology. In order to realize the full potential of these techniques, it will be necessary to understand the growth rates of bear hair and to determine the fractionations and turnover rates of sulfur in grizzly bears. Once growth rates are understood, the goal will be to sample the hair sequentially so that seasonal changes in food sources can be identified. Our data illustrate the necessity of calibrating bear-hair growth and the time required between consumption of a specific food and change in the isotopic composition of new hair. This type of study is best done with captive bears, such as the work pioneered by Dr. Charlie Robbins and his colleagues and students at Washington State University.

Conclusions

The three studies described here demonstrate how geochemical techniques widely used to investigate rocks and waters at Yellowstone can be applied to biologic problems that are associated with wildlife management.

Elements, including As, B, Be, Ce, Cl, Cs, F, Hg, K, Li, Mo, Rb S, Sb, Si, W, and other elements not described in detail here, are commonly enriched (1) in the thermal waters in the Yellowstone area, (2) in rocks altered by these waters, (3) in sinter and travertine deposits, and (4) in soils and stream sediments derived from these rocks. Although not observed or documented to date, some of these elements, such as As, F, Hg, and Mo, may be at least mildly toxic to wildlife. Many of the hydrothermally associated elements are concentrated in plant tissue and may be passed up the food chain to large animals.

The deleterious effects on wildlife of consuming hydrothermally related elements have only been established for fluorine in elk (Garrott and others, 2002). Some elements consumed by animals are essential in small amounts, some are toxic because they accumulate over time, some become toxic above a threshold level, some may weaken immune systems to the point where disease can be more easily established, and some have no apparent biologic effect and are merely excreted.

The scat of elk, bison, and moose that forage in fossil or active thermal areas show enrichments for many of the above-mentioned elements, as well as for some others. A comparison of the scat analyses with stream-sediment analyses collected in the Yellowstone area shows relatively high concentrations for 12 elements in the scat. This suite of elements includes (1) hydrothermally related elements (As, Br, Cs, Mo, Sb, and W), (2) major elements (Ca and K) that are essential elements for plants, and trace elements (Ba, Rb, and Sr) that commonly proxy for Ca or K, and (3) zinc. The behavior of zinc is not understood. It is an essential element for plants and animals

but does not normally proxy for either Ca or K. Zinc is also not related to hydrothermal activity. The uniqueness of zinc was also identified in other parts of this investigation.

Several other elements that are known to be potentially toxic to wildlife, including Cr, Hg, Ni, Pb, Se, and U, were found to be present in only very low concentrations in bison, elk, and moose scat. However, most of these elements seem to be present in elevated concentrations in one or more of the samples of (1) flesh from trout or mule deer and (or) (2) hair from grizzly bear (table 7). In the case of lead, its presence in flesh or hair and not in scat is the result of initial storage in tissue and gradual excretion in urine rather than feces (Steve Sweeney, written commun., 2002). This process may be true for one or more of the other elements as well.

The chemistry of bison and elk scat may reflect feeding habits. Comparisons of the mean and maximum values for percent ash for bison and elk scat and the values for percent ash for the sample pairs from individual sites both clearly indicate that bison ingest larger amounts of most hydrothermal elements than do elk. These larger amounts probably result from the fact that bison consume more soil substrate than do elk, as reflected in the differences in geometric mean values for percent ash for the two species.

The locations of bison- and elk-scat samples that contain anomalous amounts of hydrothermal elements show a high spatial correlation with fossil or active thermal areas or with areas immediately downstream from thermal areas. The longer that animals forage in these localities, the more likely it is that they may ingest significant amounts of potentially toxic elements such as arsenic.

The scat samples were collected Park-wide at a relatively low density. More detailed sampling in selected basins, which would include soil and forage-plant samples, as well as scat, would help to better identify the distributions, sources, and concentration levels of elements of concern in the food chains of the animal species studied.

Mercury is strongly enriched in trout tissue as compared to other sampled plants and animals of the ecosystem. Significant levels of mercury have been documented in the muscle (average 0.9 ppm, dry weight for both) and liver (average 1.6 ppm for cutthroat and 2.1 ppm for lake trout) of cutthroat and lake trout populations. These mercury levels in fish are thought to be related to sublacustrine hot-spring sources. Methylation of mercury in thermal waters is probably carried out by methanogenic or sulfate-reducing bacteria that are consumed by crustaceans such as amphipods, which are a major food source for the cutthroat trout.

The mercury levels in the cutthroat trout are transferred to the animals that eat them; thus, mercury can be used as a tracer of animal ecology. For example, bear hair collected near Yellowstone Lake has high mercury levels (0.6–1.7 ppm, dry weight), whereas the hair of bears sampled at more remote areas in the greater Yellowstone ecosystem has low mercury contents (0.006–0.09 ppm, dry weight). These data can potentially be used to quantify the percentage of the bear population that eats cutthroat trout and to determine how far individual bears travel to Yellowstone Lake to eat them. Mercury concentrations in bear hair are highest in bears that live near Yellowstone Lake. This observation provides strong evidence that mercury in grizzly bears is derived from feeding on spawning cutthroat trout in the spring and early summer and that mercury levels in bear hair can be used to trace the percentage of grizzly bears that eat spawning cutthroat trout. Additional data are needed to understand the accumulation of mercury in grizzly bears and its possible toxic effects on the bear population.

Reconnaissance stable-isotope studies of grizzly bear tissue (hair from living bears and muscle tissue from carcasses) and major foods show a large range in $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ values. The $\delta^{13}C$ values of grasses (–30.4 ‰ to –28.4 ‰) and whitebark pine nuts (–24.6 ‰ to –21.7 ‰) reflect the dominance of C_3 plants in the Yellowstone ecosystem. Fine-scale variations within these ranges may reflect the effects of elevation on enrichment factors for carbon isotopes in trees and grasses. The $\delta^{15}N$ values for grizzly bear tissue and some of their food sources show typical trophic enrichments whereby $\delta^{15}N$ values increase at each level of the food chain. The fish tissue from Yellowstone Lake, however, has anomalously high $\delta^{15}N$ values as compared to bear tissue, possibly because of the influence of thermal water on the isotopic composition of nitrogen in the aquatic food chain. The lack of significant ^{15}N enrichment in bear tissue, as compared to cutthroat trout tissue, is probably the result of two factors: (1) bear hair growth may be very slow when they are eating significant amounts of fish, and (2) a considerable percentage of bear diet is vegetable material rather than fish or animal meat.

The $\delta^{34}S$ values for the vegetation and animal tissues that have been analyzed thus far are within the range of sulfide and sulfate sulfur determined or inferred for the igneous and sedimentary rocks that underlie much of the Park. The $\delta^{34}S$ values for both cutthroat and lake trout are nearly identical to those determined for sulfate derived from thermal springs under Yellowstone Lake. Spawning cutthroat trout are enriched in ^{34}S by nearly 2 ‰ over nonspawning trout from the lake. Most of the other food sources have $\delta^{34}S$ values consistent with sulfur derived from reduced sulfur in igneous rocks. Whitebark pine nuts, however, have $\delta^{34}S$ values consistent with derivation of sulfur from sulfate in igneous rocks or possibly from Mississippian-age sedimentary rocks. Although sulfur isotopes may be fractionated during processes that occur in soils and organisms through the food chain, it is probable that the composition of both sulfate and sulfide in the food chain reflects geologic sources. If this interpretation is correct, then the $\delta^{34}S$ data support the conclusion that at least some of the grizzly bears eat whitebark pine nuts during the fall while they are growing a substantial amount of their winter hair.

We conclude that geochemical techniques commonly used to investigate geologic problems provide another tool that can be applied to biologic problems related to wildlife management. The geochemical signatures in rocks and waters in and near Yellowstone National Park that develop as a result of hydrothermal activity may provide unique tracers for studying wildlife ecology and toxicology. Integration of these geochemical techniques into specific biological studies may help address issues of interest to wildlife managers in Yellowstone National Park and the greater Yellowstone ecosystem.

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