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ELEMENT CONTENT OF RAINBOW TROUT AND SACRAMENTO SUCKER IN STREAMS OF THE GEYSERS REGION, CA

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ABSTRACT

Element Analysis was conducted on rainbow trout and Sacramento sucker muscle tissue from two streams in the Geysers area, California. Specimens were collected June 1984 in Big Sulphur Creek from sites downstream and upstream of geothermal power facilities and in Little Sulphur Creek which has no nearby geothermal development. In comparison to freshwater fish from other geographic locations, those in the Geysers area show high levels of the potentially toxic elements Hg, Pb, Zn and Cu (up to 0.7, 9.5, 47.3 and 3.1 ppm, respectively). In general, the data suggest that elevated element levels are characteristic of both Little Sulphur Creek and Big Sulphur Creek, however Zn, Cu and Pb are statistically higher in suckers collected downstream of geothermal development.

INTRODUCTION

This study provides reference data for 27 chemical elements in rainbow trout (*Oncorhynchus mykiss*) and the Sacramento sucker (*Catostomus occidentalis*), taken from Big Sulphur and Little Sulphur creeks. The terrain surrounding both streams was actively mined (primarily for mercury and manganese) prior to 1960, but only the Big Sulphur Creek watershed has undergone extensive geothermal development.

Although many elements and the compounds they produce occur naturally as a part of the normal erosion process, their concentrations can be increased during construction and operation of mines, roads, well pads, pipelines, power lines and power plants. The resultant soil exposure, steam venting from wells and

cooling tower fallout from power plants can increase element burdens in both the aquatic and terrestrial ecosystems.

MATERIALS AND METHODS

Fish muscle samples were collected from three experimental sites on Big Sulphur Creek: BIS-21.6, BIS-26.5 and BIS-30.4. (These designations refer to the distance in kilometers from the mouth of Big Sulphur Creek to the sampling site). Stations BIS-30.4 and BIS-26.5 are located upstream of the core area of geothermal development and have been less impacted by power plant and steam field development. Station BIS 21.6 is situated in the downstream portion of the watershed and has been more heavily impacted by steam field and power plant operations.

Suckers were collected from BIS-26.5 and BIS-21.6, and rainbow trout from BIS-30.4. Trout were not found in the downstream stretch of Big Sulphur Creek (BIS-21.6). The fourth collection site was located on Little Sulphur Creek, LIS-17.3. This site on Little Sulphur Creek serves as a reference location on a watershed exposed to past mining activities but no geothermal development.

For Na, K, Ca, Mg, Zn, Cu, Fe, Mn, B, Al, Si, Ti, V, Co, Ni, Mo, Cr, Sr, Ba, Li, Ag, Sr, Pb, Be and Cd three 0.8 mg subsamples of freeze-dried muscle were analyzed separately using inductively coupled plasma (ICP) emission spectrometry by the University of California laboratories in Los Angeles. Mercury and As were measured by the Babcock Laboratories in Riverside, California by atomic absorption (AA) spectrometry. Because of sample size limitation Hg and As were analyzed only once per tissue sample. Element amounts are given in parts per million (ppm) dry weight. The

lower analytical limit (LAL) defined as the lowest level of an element that can be measured with absolute certainty is given in the following: Na = 1.00, K = 150.00, Ca = 1.00, Mg = 50.00, Zn = 5.00, Cu = 0.2, Fe = 0.60, Mn = 0.10, Al = 1.00, Si = 1.00, Ti = 0.50, V = 1.00, Ni = 0.50, Sr = 0.20, Ba = 0.20, Pb = 1.00 and Hg = 0.08.

RESULTS AND DISCUSSION

Table 1 compares trout samples from BIS-30.4, which is upstream of most geothermal development, to the reference trout from LIS-17.3. Table 2 compares sucker samples

from the BIS-26.5 site which is upstream of all the older and much of the newer development, to the reference suckers from LIS-17.3. Table 3 compares sucker samples from the BIS-21.6 site, which is downstream of the most extensive geothermal development, to the reference suckers from LIS-17.3.

Boron, Ti, V, Co, Mo, Cr, Li, Ag, Sn, Be, Cd and As were below or very near the lower limit of analytical measurement for almost all the Big Sulphur Creek and Little Sulphur Creek sites. (Those chemical elements not appearing in the tables had values that were below minimum analytical limits).

Table 1. A comparison of mean element content (ppm, dry wt.) of rainbow trout muscle tissue from Little Sulphur Creek (LIS-17.3), N = 9; and Big Sulphur Creek (BIS-30.4), N = 9. An asterisk indicates the element amount was below the lower limit of accurate measurement; SD = standard deviation. Confidence level was determined by the t-test.

ELEMENTS	LIS-17.3 MEAN	LIS-17.3 SD	BIS-30.4 MEAN	BIS-30.4 SD	CONFIDENCE LEVEL
Na	4030.0	429.3	3844.8	556.5	-
K	20822.2	2491.9	18800.0	2525.4	-
Ca	1093.8	652.1	580.6	200.3	0.05
Mg	1153.5	131.2	973.4	143.5	0.05
Zn	47.3	6.7	46.9	6.3	-
Cu	1.9	0.8	2.2	0.9	-
Fe	15.5	7.3	20.7	12.9	-
Mn	0.4	0.3	0.7	0.3	-
Al	5.3	1.0	5.4	0.9	-
Si	42.5	9.1	85.3	99.7	-
Ti	0.5	0.4	1.0	0.5	-
V	*	*	1.9	1.3	-
Ni	2.1	4.0	0.4	0.2	-
Sr	3.1	1.5	2.0	0.5	-
Ba	1.1	0.6	0.6	0.2	0.05
Pb	9.5	1.5	9.2	1.9	-
Hg	0.7	0.3	0.6	0.2	-

Sodium, K, Ca, Mg and Si were found at similar levels for the suckers at LIS-17.3 and BIS-26.5 and BIS-21.6 (tables 2 and 3). Trout from BIS-30.4 and LIS-17.3 also had similar levels for Na, K, and Si, but Ca and Mg were significantly higher at the LIS-17.3 site (table 1). Whether these quantities are within normal ranges for fish in mineralized streams is unclear.

Iron, Al and Ni showed no significant differences between either species for the two streams. Quantities of Fe and Al are relatively consistent in fish muscle from both Big Sulphur and Little Sulphur creeks.

Barium levels in trout were significantly higher in LIS-17.3 compared to trout from BIS-30.4. Strontium was significantly

higher in suckers from BIS-21.6 compared to suckers from LIS-17.3.

The highest levels of Mn, 5.0 ppm, were found in suckers from BIS-21.6. This 5.0 ppm value was also significantly different from the Mn level in suckers from LIS-17.3. Detectable levels of Mn might be expected given the history of mining in the area and the presence of manganese-rich soil. Manganese does accu-

mulate in fish tissues mainly through digested food that is part of a food chain bioaccumulation (Salanki *et al*, 1982). The toxicity of this element is unclear because of the wide variation of values in published reports (*et al*, 1979).

Table 2. A comparison of mean element content (ppm, dry wt.) of Sacramento sucker muscle tissue from Little Sulphur Creek (LIS-17.3), N = 11; and Big Sulphur Creek (BIS-26.5), N = 4. An asterisk indicates the element amount was below the lower limit of accurate measurement; SD = standard deviation. Confidence level was determined by the t test.

ELEMENTS	LIS-17.3 MEAN	LIS-17.3 SD	BIS-26.5 MEAN	BIS-26.5 SD	CONFIDENCE LEVEL
Na	4130.0	523.8	3832.5	687.2	-
K	20863.6	2250.9	22275.0	4702.0	-
Ca	816.0	331.3	820.6	205.2	-
Mg	1217.7	89.2	1403.6	260.4	-
Zn	30.5	4.7	30.2	9.0	-
Cu	3.1	1.6	1.7	0.4	0.05
Fe	17.2	7.2	24.3	11.1	-
Mn	1.9	0.7	2.8	2.2	-
Al	6.4	3.0	4.9	0.3	-
Si	93.4	68.5	91.2	19.8	-
Ti	0.8	0.2	*	*	-
Ni	1.9	3.1	1.0	0.5	-
Sr	1.8	0.8	2.2	0.4	-
Ba	2.3	0.6	2.0	0.1	-
Li	0.7	0.2	0.8	0.2	-
Pb	6.1	1.2	6.5	1.0	-
Hg	0.7	0.2	0.6	0.2	-

ELEMENTS OF NOTE

The concentrations of Hg, Cu, Pb and Zn, are particularly noteworthy. Although some variation exists between streams and within species, the values for these four metals were consistently high at all sites on Big Sulphur and Little Sulphur creeks (table 4.) Comparable data on element content of the creek waters at the fish stations is not available. However, some limited data suggests that the waters of these two creeks have a relatively high level of mineralization.

High concentrations of these four metals may be toxic and/or lethal to fish. At sub-lethal levels these metals form compounds which accumulate in fish tissues. Further, mercury levels increase in concentration with succeeding levels of the food chain (biomagnification) Connell and Miller (1984).

MERCURY

In comparison to Hg levels reported in the literature, the sucker and trout muscle sampled in this study contained moderately high levels of Hg. Mercury concentrations were very similar for both fish species on Little Sulphur Creek (sucker, 0.7 ppm; trout, 0.7 ppm)

and for the BIS-26.5 (sucker, 0.6 ppm) and BIS-30.4 (trout 0.6 ppm) sites on Big Sulphur Creek. The only mean value for either species below 0.5 ppm (the USDA standard for human consumption) was the sucker sample collected downstream at BIS-21.6 (0.4 ppm).

Uthe and Bligh (1971) examined lake whitefish, northern pike, rainbow smelt and yellow perch from industrialized areas in Canada and found Hg levels to vary from 0.07 ppm to 0.70 ppm, respectively, in dressed fish (muscle and bone). Benson *et al* (1976) examined 160 fish representing 19 species from Idaho reservoirs and the Snake River. Ninety-eight percent of the samples contained detectable Hg, with the highest residues over 6.0 ppm; 19 percent contained residues over 0.5 ppm.

In fish, Hg is accumulated in direct proportion to fish weight, fish length and duration of exposure (Scott and Armstrong, 1972; Scott, 1974). Our data show a clear relationship of Hg content to weight. Small suckers (less than 100 g each) collected from BIS-21.6 were found to have mean Hg levels of 0.28 ppm, while large suckers (100 g or more) had a mean Hg level of 0.58 ppm. Moreover, Hg has been shown to concentrate in fish high in the food chain particularly in large predatory fish (Wissmath and Kreuzer, 1979). Olson *et al* (1975) have shown that there is a pronounced ability to take in Hg and a concomitant limited capacity to excrete this metal. This inability to eliminate Hg results in levels above 1.0 ppm accumulating in fish tissues collected from water containing as little as 0.018 ppm of the organic form, methylmercury (Olson *et al*, 1975).

Table 3. A comparison of mean element content (ppm, dry wt.) of Sacramento sucker muscle tissue from Little Sulphur Creek (LIS-17.3), N = 11; and Big Sulphur Creek (BIS-21.6), N = 11; SD = standard deviation. Confidence level was determined by the t-test.

ELEMENTS	LIS-17.3 MEAN	LIS-17.3 SD	BIS-21.6 MEAN	BIS-21.6 SD	CONFIDENCE LEVEL
Na	4130.0	523.8	3829.4	851.4	-
K	20863.6	2250.9	18690.9	2899.5	-
Ca	816.0	331.3	953.1	485.3	-
Mg	1217.7	89.2	1135.7	159.8	-
Zn	30.5	4.7	37.0	5.9	0.01
Cu	3.1	1.6	2.0	0.9	-
Fe	17.2	7.2	18.2	8.1	-
Mn	1.9	0.7	5.0	2.4	0.01
Al	6.4	3.0	5.6	1.3	-
Si	93.4	68.5	80.4	29.6	-
Ti	0.8	0.2	9.0	13.7	-
Ni	1.9	3.1	1.9	3.4	-
Sr	1.8	0.8	3.6	1.4	0.01
Ba	2.3	0.6	1.6	0.6	-
Li	0.7	0.2	0.7	0.3	-
Pb	6.1	1.2	8.7	1.2	0.01
Hg	0.7	0.2	0.4	0.2	0.05

Table 4. Mean concentrations (ppm, dry wt.) of Hg, Zn, Cu, Pb for Sacramento sucker (N = 11) and rainbow trout (N = 9) musculature from Little Sulphur Creek (LIS-17.3) and the upstream (BIS-30.4) and downstream (BIS-21.6) sites of Big Sulphur Creek. Values in parentheses are standard deviations; an asterisk means trout were not present.

SPECIES	SITE	HG	ZN	CU	PB
Sucker	LIS-17.3	0.7 (0.2)	30.5 (4.7)	3.1 (1.6)	6.1 (1.2)
Trout	LIS-17.3	0.7 (0.3)	47.3 (6.7)	1.9 (0.8)	9.5 (1.5)
Sucker	BIS-26.5	0.6 (0.2)	30.2 (9.0)	1.7 (0.4)	6.5 (1.0)
Trout	BIS-30.4	0.6 (0.9)	46.9 (6.3)	2.2 (0.9)	9.2 (1.9)
Sucker	BIS-21.6	0.4 (0.2)	37.0 (5.9)	2.0 (0.9)	8.7 (1.2)
Trout	BIS-21.6	*	*	*	*

LEAD

Mean Pb concentrations recorded for this study were high when compared with those reported in the literature. Concentrations varied between species; however, the difference was consistent for both Little Sulphur Creek (sucker, 6.1 ppm; trout, 9.5 ppm) and BIS-30.4 (trout, 9.2 ppm) sites on Big Sulphur Creek. Lead levels were significantly higher in suckers (8.7 ppm) from the BIS-21.6 site.

Pakkala *et al* (1972) measured whole body concentrations and found no obvious relationship between fish size, species or sex and their respective Pb, Zn and Cu concentrations. They also measured Pb concentrations from 419 fish from 49 different bodies of water in New York state. Whole body concentrations of Pb ranged from 0.3 ppm to 1.5 ppm with a few samples measured at 3.0 ppm. Uthe and Bligh (1971) measured Pb concentrations in dressed samples of lake whitefish, northern pike, rainbow smelt and yellow perch from lakes near industrialized and non-industrialized areas and recorded values below 0.5 ppm. Badsha and Goldspink (1982) examined bream and roach from north-western England and found Pb levels in muscle that ranged from 0.17 to 1.55 ppm, while kidney, liver and bone had concentration values that in many cases exceeded 10 times those of muscle alone.

ZINC

Zinc levels in fish musculature from Big Sulphur and Little Sulphur creeks are generally much higher than those reported in the literature. Concentrations varied between species; however, the difference was consistent for both Little Sulphur Creek (sucker, 30.5 ppm; trout, 47.3 ppm) and BIS-26.5 (sucker, 30.2 ppm) and BIS-30.4 (trout, 46.9 ppm) on Big Sulphur Creek. Zinc concentrations were significantly higher for suckers at BIS-21.6 on Big Sulphur Creek.

Wilson *et al* (1981) analyzed rainbow trout muscle and liver tissue for Zn concentrations due to acid mine wastes in the Sacramento River Basin. They found no relationship between metal concentrations in the muscle and the size or age of trout. Further, neither was there a relationship to the concentration of Zn in the water. They concluded that the observed range of Zn (8.3 to 15.3 ppm, dry weight) was similar to other studies and was a "background" level for muscle. The muscle level concentrations for trout in the present study were three to five times the assumed "background" level. Wilson *et al* (1981) found Zn concentrations in liver tissues to increase with fish length, weight and age. In their study the range of Zn in liver was from 116 to 190 ppm which is minimally a ten-fold increase over the muscle concentration. On a comparative basis, the rainbow trout livers in

the present study (had they been analyzed) would have had an estimated liver Zn level of about 460 ppm.

Largemouth bass from the Savannah River in South Carolina were found to have muscle concentrations of 22.2 ppm Zn (Pinder and Giesy, 1981). Four species of dressed fish from Canadian lakes ranged from 12 ppm in lakes free from industrial development to 20 ppm near industrialized regions (Lucas *et al*, 1970). Badsha and Goldspink (1981) found that Zn values for muscle tissue from bream and roach in northwestern England ranged from 1.49 to 11.45 ppm.

COPPER

Copper values for muscle in suckers and trout were higher than those reported in the literature. Copper concentrations varied in suckers at Little Sulphur Creek (3.1 ppm) and BIS-26.5 (1.7 ppm) and BIS-21.6 (2.0 ppm) on Big Sulphur Creek. The higher value for Cu on Little Sulphur Creek was significant; however, copper levels for trout were similar for Little Sulphur Creek (1.9 ppm) and the BIS-30.4 Site (2.2 ppm) on Big Sulphur Creek.

Copper is one of the most toxic metals affecting fish, with a wide range of sublethal and lethal values (Black *et al*, 1976). Water hardness and pH can also significantly modify the toxicity of Cu.

Wilson *et al* (1981), in addition to analyzing rainbow trout muscle and liver tissues for Zn in the Sacramento River Basin, also obtained Cu data. As with Zn, there was no relationship between concentrations in the muscle and size or age of the trout; nor was there any relationship to Cu levels in the water. Again, as with Zn, Cu levels had a range of "background" levels similar to other studies in the continental United States, namely, <0.6 to <1.0 ppm (dry weight).

Largemouth bass muscle from the Savannah River in South Carolina had Cu concentrations of 0.62 ppm (Pinder and Giesy, 1981). Four species of Canadian dressed freshwater fish had Cu concentrations that varied from 0.5 ppm in relatively unpolluted areas to 1.28 ppm in highly industrialized areas (Uthe and Bligh, 1971). Whole fish

values for Lake Superior, Lake Michigan and Lake Erie ranged from 0.85 ppm to 2.7 ppm (Uthe and Bligh, 1971).

ELEMENT LOADS

Both natural and anthropogenic activities have contributed to the element load of fish in Big Sulphur and Little Sulphur creeks. Until the early 1960's mercury mines represented the dominant anthropogenic activity in both drainages. Found in the same ores deposits with mercury are Cu, Zn, Mn and Pb. Surface mining usually creates acidified, mineral-rich deposits that are readily eroded and eventually accumulate in the hydrosphere (Connell and Miller, 1984).

Geothermal steam production has steadily increased in the Geysers since 1960. Many parts of the process leading to electricity production allow for the release of mineral-laden steam into the atmosphere. The dissolved and particulate matter returns to the earth as fallout and eventually enters the hydrosphere. Soil erosion, from the many construction phases of steam development, may also have accelerated the release of metals into the environment. It is probable that both the Little Sulphur Creek and Big Sulphur Creek drainages have historically carried a high trace element content. The rock formations at the Geysers are prone to erosion, and natural weathering of rock and soil may maintain a high background element load in both streams. In addition, there are, at least in the Big Sulphur Creek area, a number of natural geothermal surface features (hot springs and fumaroles) that contribute mineral-laden steam and water to the environment.

Assessing the potential hazard of these elements to fish populations at the Geysers would be conjectural based on this initial survey and limited sample size. Certainly many trace elements, at less than toxic levels, are essential for normal physiological processes (Lucas *et al*, 1970). At the other extreme, high concentrations of a particular element can be toxic. (See Bryan, 1976, for limitations of lethal toxicity data in metal studies.) Chronic exposure to sublethal concentrations of elements can debilitate growth and reproduction of fish Benoit *et al*, 1976;

Brungs, 1969; Davies *et al.*, 1976; Eaton, 1973; Holcombe *et al.*, 1979 Pickering and Gast, 1972; Spehar, 1976). Subtle changes in one or more element concentrations can affect enzyme relationships (Davies, 1976). Seemingly unimportant levels of one element may act synergistically with another element to cause an effect. Moreover, physical changes in water temperature, pH, hardness and redox conditions modify element toxicity (Connell and Miller, 1984).

It is known that many fish species can acclimatize to enriched levels of various elements. The different species' total physiological and behavioral response vary seasonally and geographically as well as according to the individual's age and weight when first exposed (Connell and Miller, 1984).

CONCLUSIONS

Historically both Big Sulphur and Little Sulphur creeks have probably maintained high background levels of many chemical elements. Trout and suckers from both streams exhibit high levels of Hg, Zn, Cu and Pb when compared to freshwater fish from other geographic locations. The conservative measure of muscle tissue of Big Sulphur Creek suckers shows enrichment of Zn, Cu and Pb, compared to those from Little Sulphur Creek. Further, the elevated levels in suckers were from fish living downstream of geothermal development and natural geothermal surface features. Of the four elements, Hg is probably of greatest concern since Hg is known to bioaccumulate, which means that this heavy metal is transferred and concentrated in the food chain.

There are critical thresholds in the physiology of all species and in the ecological balance of an aquatic community. Trout and non-game species of fish have probably adapted to many of the environmental extremes of Big Sulphur and Little Sulphur creeks. Because of these extremes, the Big Sulphur Creek drainage is a stressed environment. Whether geothermal power development adds significantly to the stress is not clear. Further studies and monitoring will be necessary to adequately answer this question.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the efforts of Steven J. Sharpe, Sonoma County Department of Planning who's patience and administrative efforts were instrumental in completing this study. This work was supported by a grant from the California Energy Commission and conducted with the cooperation of the geothermal industry. The processing of tissues and data entry were the excellent contribution of Kathy Ward Jennings and Rebecca Banks from the Institute of Chemical Biology.

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