

Metal Absorption by *Equisetum* (Horsetail)

GEOLOGICAL SURVEY BULLETIN 1278-A



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By HELEN L. CANNON, HANSFORD T. SHACKLETTE, and HARRY BASTRON

CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING
FOR MINERALS

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*A study of the metal content of
horsetail plants as related to
the amounts of metals in the
soil on which they grew*



UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

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METAL ABSORPTION BY *EQUISETUM* (HORSETAIL)

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ABSTRACT

Samples of *Equisetum* (horsetail) have been collected from a variety of mineralized and unmineralized areas throughout the conterminous United States and Alaska and analyzed for 28 elements to determine whether this primitive plant is an accumulator of metals.

The metal content of *Equisetum* collected from 15 mineralized areas was generally lower than that of other plants growing there. Gold contents in the ash of *Equisetum* averaged only 0.17 part per million in the conterminous United States and 0.54 part per million in Alaska. Early reports of large amounts of gold in *Equisetum* may be erroneous; a study of the analytical procedures that were used suggests that other metals, in addition to gold, were measured and reported as amounts of gold.

Equisetum consistently accumulates zinc in amounts greater than are in the substrate; commonly these amounts are also greater than those in other plants that grow in the same soil. *Equisetum* is, therefore, an accumulator of zinc but, contrary to earlier reports, is not an accumulator of gold.

INTRODUCTION

The purpose of this study was to determine whether species of *Equisetum* are accumulators of metals, as suggested by the high gold values reported in these plants (Nemec and others, 1936). Samples of *Equisetum* (horsetail, scouring rush) for this study were collected throughout the conterminous United States and Alaska, largely from mineralized areas, and analyzed for 28 elements. The samples were collected and analyzed at intervals over a long period of time, but only recently have sensitive analytical methods for gold in plants been available.

The genus *Equisetum* includes about 25 species and is found throughout the world except in Australia and New Zealand (Core, 1955, p. 222). Some species grow in ponds and marshes, some in damp shady places, and some in relatively dry sites (Smith, 1938, p. 235). They are commonly abundant around tailings ponds in mining districts. The

plant is made up of annual or perennial aerial stems 10–20 cm high that arise from a deep-seated perennial rhizome. The stems are cylindrical and jointed, and the minute leaves unite to form a sheath at each node. Reproduction is by means of spores that are borne in conelike structures produced at the tips of the stems (fig. 1). The root system commonly is extensive; *Equisetum sylvaticum* growing on the tundra was found by Malyuga (1964, p. 72) to have roots at a depth of 150 cm where permafrost occurred at a depth of 60 cm.

Some species of horsetails were used as scouring rush in pioneer days, and all species have a high content of silica and are rough to the touch. *Equisetum arvense* has been found to have a poisonous effect on grazing stock when it occurs in any quantity in hay or pasturage, according to Benedict (1937, p. 1126) and others. Both aconitic acid and the alkaloid equisetin, which is a nerve poison, have been identified in this plant (Tehon and others, 1946). However, Porsild (1951, p. 67) wrote, "The species is of considerable importance to wildlife; the green, sterile plant and also the starch-filled root-tubers furnish an important food supply for a large number of herbivorous mammals and birds." Some Eskimos and other native people of Alaska refer to this and other species of *Equisetum* as "goose grass" because the young shoots are avidly eaten by large flocks of wild geese in early spring.

The scientific and common names of the species of *Equisetum* that are discussed in this report are (Fernald, 1950):

- Equisetum arvense* L., common or field horsetail
- E. fluviatile* L.,¹ water horsetail
- E. hyemale* L., scouring rush
- E. hyemale* var. *robustum* (A. Br.) A. A. Eat., scouring rush
- E. kansanum* Schaffn., Kansas horsetail
- E. limosum* L.,¹ water horsetail
- E. litorale* Kohlewein, shore horsetail
- E. palustre* L., marsh horsetail
- E. pratense* Ehrh., meadow horsetail
- E. sylvaticum* L., woodland horsetail
- E. telmateia* Ehrh., giant horsetail
- E. variegatum* Schleich., variegated horsetail

Samples were collected in as many types of mineral districts as possible and also in unmineralized areas for comparison. Plants

¹ The synonymy of *E. fluviatile* and *E. limosum*, two closely related species, is confused; each is considered to be a form or variety of the other by different writers.

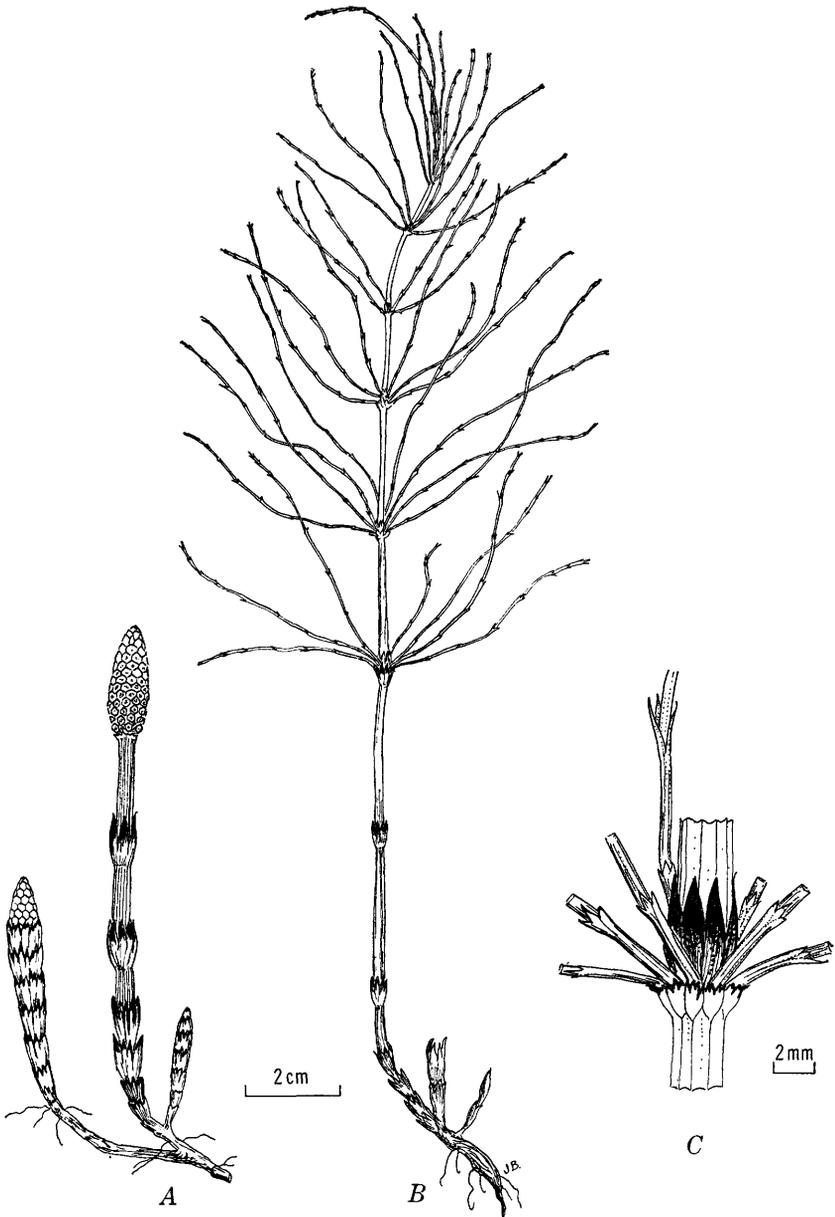


FIGURE 1.—*Equisetum arvense* L., field horsetail. *A*, Fertile stems bearing spore-producing cones (strobili). *B*, Sterile stem with part of rhizome, young stems, and roots. *C*, Node of sterile stem with cylindrical toothed sheath and whorl of branches.

were collected, therefore, from areas mineralized with antimony, copper, gold, iron, lead, mercury, molybdenum, silver, tungsten, uranium, vanadium, and zinc.

PREVIOUS WORK

The chemical composition of the siliceous scouring rush has interested many workers since 1870, but actual analyses of samples of the genus are relatively rare. (See table 1.) Wolff (1871, 1880) and Mariani (1888) published analyses for major constituents in the ash of *Equisetum arvense* and *E. telmateia*. The results are not unusual except for the large percentages of silica, in which respect horsetails resemble grasses. The high iron values reported by Mariani were probably due to contamination from iron vessels. Dieulafait (1885) found a mean of 12.0 percent potassium sulfate and 14.3 percent calcium sulfate in 168 samples of *Equisetum* ash. Thus, as these primitive plants use sulfates rather than carbonates in their metabolic processes, he proposed that the sulfur in the Coal Measures was derived from *Equisetum*.

Bateman and Wells (1917) studied the tolerance of various species of plants to the tailings ponds of the Anaconda smelter. *Equisetum variegatum* was one of the more tolerant plants to grow there and contained 296 ppm (parts per million) copper in the ash, although other species more restricted in distribution contained as much as 6,210 ppm. Vogt, Braadlie, and Bergh (1943) analyzed *E. arvense* growing on a sulfide copper deposit and found 43 ppm copper, 16 ppm lead, 4,800 ppm zinc, 140 ppm manganese, and 380 ppm iron. These values, except that for zinc, are considerably below average for plants. Robinson, Lakin, and Reichen (1947) found *Equisetum* to accumulate more zinc than any other genus growing on the zinc slime ponds at Friedensville, Pa. A maximum value of 7,000 ppm dry weight (approximately 3.2 percent in the ash) was reported for 14 unwashed samples; the average was 4,000 ppm. A sample collected close to the one having the maximum value and brushed very carefully contained 3,200 ppm, but a washed sample contained only 1,900 ppm. Apparently two-thirds of the metal in ash of unwashed plants from highly contaminated areas can be discounted as dust clinging to the plant.

Lovering and Engel (1968) have recently conducted greenhouse experiments with *Equisetum* and three grasses. Plants were grown in pots of basalt and rhyolite and fed a nutrient solution. Silicon and other elements were absorbed from the ground rock by both grasses and *Equisetum* although not in normal quantities. The silicon was shown to be translocated to the above-ground parts of the *Equisetum* as an

organic complex, aromatic in nature, and to be precipitated in the cell walls as plant opal.

Equisetum has attracted much attention as a reported plant accumulator of gold since 1936 when Nemeč, Babička, and Oborsky obtained 610 ppm gold in the ash of *E. palustre* that had grown in soil containing only 0.2 ppm. Other plants collected from the same area also had exceptionally large amounts of gold. These values have been quoted by several other workers (Benedict, 1941; Lundberg, 1941; Thyssen, 1942; Malyuga, 1964).

In view of the values that have been reported from other areas since 1936, it might be well to review in detail the collection and analytical data of these particular samples. Babička (1943) gave, in his report "Gold in living organisms," a full account of the investigation begun by Nemeč and Babička in 1935.

Near the village of Oslany in old Slovakia, andesite and rhyolite containing 0.1 gram gold per ton are weathered to gravels and clays enriched to 0.2 gram gold per ton. The gold is believed to occur as colloidal gold because it has never been observed in the metallic state; this fact is considered by Babička to be significant to the phenomenon of unusual gold accumulation by plants. The gold was originally found in 1934 in corn being grown in the area, and a long investigation was commenced. Research on analytical methods resulted in an original colloid-pectin method. In 1935, samples of *Equisetum palustre*, the swamp horsetail, and *E. arvense*, the field horsetail, were collected, and control samples were collected from the nearby village of Hornia Ves. The samples were air dried and then ashed at very low temperatures in porcelain dishes. The ash was dissolved in aqua regia, and the solution was then evaporated. The residue was treated with hydrochloric acid, and the solution was boiled to precipitate silicic acid and then was filtered. The dilute hydrochloric acid filtrate was treated with hydrogen sulfide to precipitate the acid-insoluble sulfides, apparently considered by the authors to be solely gold sulfide. If the amount of precipitate was large, it was then weighed directly; if small, the residue was put into solution and the gold was precipitated, using pectin as a protective colloid, and measured colorimetrically against standards. It should be pointed out that a group of metals would be precipitated by this method, and direct weighing of the residue would include the sulfides of copper and several other metals. Thus the high values of 611 ppm gold in *E. palustre* and 63 ppm in *E. arvense* may be erroneous.

The *Equisetum* samples from Oslany and Hornia Ves, which were analyzed for major constituents as well as for gold, contained large amounts of aluminum and silica. The silica content varied consider-

TABLE 1.—Some analyses of *Equisetum*

[Converted from oxide and from dry weight to approximate ash values where necessary. Number in Leaders (...) indicate

Year	Author	Sample localities	Species	Ash content (percent)	Al (percent)	Ca (percent)	Cl (percent)	Mg (percent)	P (percent)
1871	Wolff ¹		<i>arvense</i>	18.7		12.15		1.69	1.22
			<i>telmateia</i>	26.7		6.14		1.09	.62
1888	Mariani ¹		do	17.39	0.51	9.65	6.12	1.32	.55
			<i>arvense</i>	6.05		14.16	5.49	4.16	1.26
1917	Bateman and Wells.	Copper tailings, Montana.	<i>variegatum</i>						
1936	Nemeč, Babička, and Oborsky. ²	Oslany, Slovakia.	<i>palustre</i>	21.65(*)	.99(*)	5.76(*)	5.42(*)	1.23(*)	.70(*)
1943	Babička	Oslany, Slovakia, on andesite clays.	<i>hyemale arvense</i>	23.35(*)	2.30(*)	5.53(*)	5.30(*)	1.63(*)	1.01(*)
		Grossen, Schutt Insel on Danube alluvium.	do		2.1(*)	3.60(*)		1.76(*)	
1943	Vogt, Braadlie, and Berghs	Copper-sulfide deposit in Rørosfeltet.	do	25.0					
1945	Robinson and Edgington.		do						
1947	Robinson, Lakin, and Reichen.	Friedensville, Pa., slime ponds containing anomalous amounts of Zn, Pb.	do						
		Background.	do	31.1(2)					
1950	Warren and Delavault.	Clinton district, British Columbia (Au).	do	16.70					
		do	do	17.20					
		do	do	18.00					
		do	do	22.75					
1963	Razin and Roshkov.	Aldan Shield, U.S.S.R.	<i>pratense</i>						

¹ The values have been converted from the oxides.² Quoted by McMurtrey and Robinson (1938), Lundberg (1941), Thyssen (1942), and Babička (1943).

ably; a maximum content of 83.5 percent SiO₂ was found in older plants. Individual species had consistently high contents of Al₂O₃.

Several species of plants were then studied from a second area at Grossen Schutt Insel, on the Danube River. The alluvial deposits on which these plants grew were also derived from andesite and contained more than 0.2 gram gold per ton. The gold, which occurred both as colloidal gold and as coarser particles, diminished with depth. *Equisetum arvense* was sampled several times during the year to determine its average composition. The samples contained an average of only 16 ppm gold in the ash of aerial parts. Babička believed that the value was lower at this locality than at Hornia Ves because the gold is coarser and, thus, is not as readily absorbed by plants. On the other hand, the gold analyses were made by J. Splichal in a laboratory set

ash reported in the literature

parentheses is number of samples averaged; asterisk (*) signifies average of many samples.
no data available]

K (per- cent)	Si (per- cent)	Na (per- cent)	S (per- cent)	Cu (ppm)	Au (ppm)	Fe (ppm)	Pb (ppm)	Mn (ppm)	As (ppm)	Ti (ppm)	Zn (ppm)
15.90	41.7	0.37	4.00	-----	-----	4,900	-----	-----	-----	-----	-----
6.64	32.97	.44	1.12	-----	-----	9,800	-----	-----	-----	-----	-----
7.69	14.51	1.05	3.58	-----	-----	163,500	-----	-----	-----	-----	-----
3.53	2.89	5.73	2.71	-----	-----	261,000	-----	-----	-----	-----	-----
-----	-----	-----	-----	296	-----	-----	-----	-----	-----	-----	-----
12.46(*)	28.58(*)	.56(*)	1.06(*)	-----	*610(*)	8,300(*)	-----	-----	-----	-----	-----
-----	33.1(*)	-----	-----	-----	-----	-----	-----	150-10,000(*)	-----	-----	-----
16.35(*)	23.45(*)	.59(*)	1.44(*)	-----	*63(*)	21,000(*)	-----	-----	-----	-----	-----
21.58(*)	37.22(*)	1.07(*)	-----	80(*)	*16(*)	24,900(*)	-----	-----	-----	12,000(*)	2,700(*)
-----	-----	-----	-----	43	-----	380	16	140	-----	-----	4,800
-----	32.7(*)	-----	-----	-----	-----	-----	-----	-----	-----	-----	18,440(14)
-----	-----	-----	-----	-----	.34	-----	-----	-----	-----	-----	522(2)
-----	-----	-----	-----	-----	.17	-----	-----	-----	-----	-----	-----
-----	-----	-----	-----	-----	.34	-----	-----	-----	-----	-----	-----
-----	-----	-----	-----	-----	.33	-----	-----	-----	1.0	-----	-----
-----	-----	-----	-----	-----	.4(8)	-----	-----	-----	-----	-----	-----

* Soil contained 0.2 ppm gold.

up in the Kolozs-Nema area, in the plant-physiology institute of the Karls University in Czechoslovakia and in the Geological Institute in Prague. These analyses presumably were made by orthodox methods, so that the separation of gold from the associated metals may have been more nearly complete. In the samples of *Equisetum* that have been analyzed more recently and reported by other workers, no such high values have been obtained; in fact, no sample has contained more than 1 ppm gold in the ash. Four samples collected by Warren and Delavault (1950) in the Clinton district of British Columbia contained from 0.17 to 0.34 ppm gold in the ash. Eight samples from the Aldan shield, U.S.S.R., analyzed by Razin and Rozhkov (1963), contained an average of 0.4 ppm gold.

OBJECTIVES AND METHODS

The collection of *Equisetum* in various types of mineralized environments and the spectrographic analyses of the material were proposed for two reasons. First, the information available in the literature suggested that this primitive plant might be a remarkable accumulator of metals; second, analysts of the U.S. Geological Survey spectrographic laboratories believed that the ashed plant material would be especially amenable to analysis by their spectrographic techniques for rocks, minerals, and other materials (Bastron and others, 1960; Myers and others, 1961) because of the high silicon content.

The data presented here were not collected at a single time as a part of an organized project but as the opportunity permitted over a period of nearly 20 years. The samples, collected largely by Helen Cannon and Hansford Shacklette, were all taken from above-ground parts but were not washed. The samples were ashed at temperatures not exceeding 450°C. Most of the minor-element analyses were performed by Harry Bastron using emission spectrography; a few major elements were analyzed chemically, and the gold values, which are below the usual limits of spectrographic detectability, were obtained by Thelma Harms using an atomic-absorption method developed by Thompson, Nakagawa, and VanSickle (1968) for geologic materials.

UPTAKE AND CONCENTRATION OF METALS BY EQUISETUM

Concentrations of 21 elements in the ash of *Equisetum*, collected from unmineralized and mineralized ground throughout conterminous United States, were obtained by spectrographic and chemical analyses as shown in table 2. Contents of tin, lanthanum, beryllium, scandium, yttrium, and ytterbium were below the sensitivity of the method. Contents of copper, molybdenum, lead, zinc, and manganese were greater in samples from mineralized ground than in background samples.

NORMAL CONCENTRATIONS OF METALS IN EQUISETUM

Equisetum growing in unmineralized ground generally has a lower percentage of metals than the average for all types of vegetation as shown in table 3.

A plant such as *Equisetum* that accumulates silicon in its tissues will yield more ash per unit of dry weight than will a plant with a lower silicon content. For this reason, the percentage of a metal that is reported in *Equisetum* ash may be lower than that in the ash of average vegetation, although the actual amounts in dry weight of *Equisetum* may be average.

ANOMALOUS METAL CONTENTS IN EQUISETUM FROM MINERALIZED AREAS

The metal content of *Equisetum* collected from 15 mineralized areas was surprisingly low and in many samples did not equal that of other plants growing in the same environment (table 3).

The highest lead, zinc, and molybdenum contents occurred in *Equisetum* collected from districts where these respective metals were mined commercially. The highest chromium, titanium, and zirconium contents occurred in plants collected as background material at Kenwood Beach, Va., and Jones Wharf, Md.

Many of the other metals in *Equisetum* showed little correlation with the major economic metal of the area. The uptake of these metals by *Equisetum* may depend upon the solubility of the metal and the pH of the soil rather than on the total amount of metal that occurs there.

ORE HILL MINE

A comparison between the uptake of copper, lead, and zinc by *Equisetum* from a sulfide-ore environment and that by other types of plants was made at the Ore Hill mine, Warren, N.H. The mine lies at an elevation of 1,600 feet, in the White Mountain National Forest, about 3½ miles west of Warren. It was originally opened for copper in 1840, but zinc was found to predominate at a depth of 150 feet, and the mine was worked intermittently until about 1922 for zinc and the byproducts copper, lead, and iron. The ore contained black sphalerite mixed with copper, lead, and iron sulfides and occurred in heavily sheared schist near the base of the Ammonoosuc Volcanics.

The top few inches of surface soil and tailings that were sampled contained more lead than either copper or zinc, but a comparison with fresh samples of the tailings collected at a depth of 4 feet by the U.S. Bureau of Mines (C. L. Rogers, 1943, unpub. data) showed that all three metals are largely leached from the surface soils, and that zinc predominates at depth. The two *Equisetum* collections contained small amounts of copper but large amounts of lead and very large amounts of zinc (table 4). The chlorotic *Equisetum* sample contained more zinc than the sample of birch or the algae that grew in a highly mineralized stream. Undoubtedly *Equisetum* is an accumulator of zinc.

TABLE 2.—*Accumulation of elements by Equisetum in the conterminous United States, in parts per million of ash*
 [Analysts: Harry Bastron, C. S. Papp, G. H. VanSickle, and J. G. Watterson. Leaders (....) indicate no data available]

Sample No.	Locality	Collection data	Elements in the substrate in excess of background values	Species	Collector	Ash content (per cent)
150842	Ely, Orange County, Vt.	Tailings from ore in altered volcanics.	Cu.	arsense.	H. L. Cannon.	33.7
150843	do.	On undisturbed ground near shaft.	Cu.	arsense.	do.	29
150844	Warren, Grafton County, N.H.	Tailings.	Cu, Zn, Pb, Ag	do.	do.	35.9
150845	do.	Outcrop of acid schist.	Cu, Zn, Pb, Ag	do.	do.	33.2
150846	Franklin, Sussex County, N.J.	Limestone mine dumps.	Zn, Fe, Mn.	do.	do.	18.6
150848	Vancluse, Orange County, Va.	Quartz veins.	Au.	do.	do.	21
150850	Kearsarge, Houghton County, Mich.	Purified plant ash (a)	Cu.	sylyticum.	do.	19.4
do.	do.	Mineral contaminant (b)	Cu.	do.	do.
do.	do.	Unrefined sample (a+b)	Cu.	sylyticum?	do.
150851	Manning, Orleans County, N.Y.	Undrained North Oak Orchard bog, mineralized.	Zn, Pb.	arsense.	do.	20.2
150852	do.	Drained Oak Orchard muck, mineralized.	Zn, Pb.	fluviatile.	do.	20.9
150853	do.	Undrained bog south of Albion, unmineralized.	None	arsense.	do.	18
150856	Friedensville, Lehigh County, Pa.	Limestone tailings.	Zn.	do.	do.	22
150857	Nederland, Boulder County, Colo.	Tungsten mill tailings.	W.	titorale.	do.	33.3
150858	Chimax, Lake County, Colo.	Below upper tailings pond.	Mo, W.	arsense.	do.	18.9
150861	Black Hawk, Gilpin County, Colo.	Alluvium below Black Cat mine.	Au.	do.	do.	28.4
150864	do.	Over quartz veins.	Au.	do.	do.	24.2
150865	Slick Rock, San Miguel County, Colo.	River alluvium below mill.	V, U.	do.	do.	24
150866	Santa Fe Creek, Santa Fe County, N. Mex.	Limbergitte dike.	Cu, Fe, U.	pratense (c)	do.	30.7
150862	Bigck Canyon Spring, Jerome, Yavapai County, Ariz.	Spring in andesite.	Cu.	variegatum.	do.	27.1
150863	Kokono, Summit County, Colo.	Hillside bog, unmineralized.	None	arsense.	Mary Durrell.	22.6
150860	Gothenberg, Dawson County, Neb.	Miocene sediments.	do.	pratense.	H. L. Cannon.	32.2
150869	Triplato Basin, Summit County, Colo.	Granite glacial till.	do.	do.	do.	21
150875	Falls Church, Fairfax County, Va.	Wissahickon Schist.	do.	(c)	W. O. Robinson.	21.5
150876	Kenwood Beach, Hanover County, Va.	Tertiary sands.	do.	(c)	do.	41.7
150874	Jones Wharf, Worcester County, Md.	do.	do.	arsense.	S. F. Blake.	38.5
150847	Bandung, Grafton County, N.H.	Iron schists.	do.	arsense.	H. L. Cannon.	22.6
58-375	Utley, Henderson County, Ky.	Loess over sandstone.	do.	hyperite var. robustum.	H. T. Shacklette	16.5

Sample No.	Ag	Al	Au	B	Ba	Co	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	P	Pb	Sr	Ti	V	Zn	Zr
150342	0.6	1,300	0.1	130	270	6	0	100	300	14,000	460	0	300	26	4,800	5	50	46	10	900	0
150343	0.4	860	.2	160	540	2	0	36	370	16,000	40	12	1,800	5	9,200	58	350	62	40	300	0
150344	1.2	3,400	.1	270	680	0	1	140	1,800	11,000	170	5	1,200	3	5,200	350	720	140	30	3,400	10
150345	1.6	5,000	<.1	210	900	0	2	120	2,600	14,000	90	6	2,200	4	4,800	420	460	200	30	7,200	20
150346	.4	1,300	.1	190	400	0	3	50	1,200	22,000	1,000	65	800	0	11,000	18	230	88	20	2,800	0
150348	1.0	4,800	.1	80	360	6	12	72	6,200	50,000	1,400	7	10,000	4	16,000	11	860	800	40	0	50
150350	1	1,300	(1)	190	230	0	8	400	4,200	18,000	1,110	7	7,200	5	8,400	18	1,000	660	40	400	10
	5	34,000	(1)	1,300	380	37	140	1,900	95,000	32,000	2,200	5	11,000	63	0	30	40	14,000	280	1,400	420
	1	7,700	(1)	300	240	4	20	550	13,000	19,000	320	7	7,600	11	7,600	19	900	2,000	60	500	50
150351	1	820	(1)	260	300	0	4	40	410	50,000	180	5	1,700	0	7,300	16	120	60	30	1,000	0
150352	1	640	(1)	260	230	3	2	42	500	26,000	1,000	11	3,400	0	12,000	83	130	58	30	1,300	20
150353	(1)	100	(1)	200	200	0	3	10	320	26,000	60	0	500	4	6,000	7	60	48	20	1,100	0
150356	1	1,300	(1)	140	640	0	8	94	1,000	35,000	50	5	900	4	6,700	18	300	100	10	9,000	0
150357	(1)	7,500	.1	340	800	3	13	160	5,100	21,000	800	8	10,000	6	4,600	22	1,000	510	30	0	30
150358	(1)	6,200	.1	610	680	12	7	240	4,300	27,000	29,000	150	6,400	280	8,000	90	1,300	470	50	1,200	30
150361	.6	4,000	.2	350	480	0	0	140	120	19,000	140	0	4,000	0	3,600	12	80	42	10	300	0
150364	.8	1,500	.2	420	390	0	7	160	1,400	5,800	1,100	0	1,600	80	3,600	58	900	100	20	3,900	20
150365	.7	900	.1	460	640	2	1	300	5,000	10,000	1,000	5	4,400	4	4,800	11	1,000	76	30	700	10
150366	(1)	9,000	.2	360	580	4	10	270	5,900	7,500	1,000	0	2,800	22	7,300	9	120	660	20	200	40
150362	(1)	540	.2	280	150	3	1	600	320	11,000	140	0	4,500	6	10,000	7	10	150	10	300	0
150363	(1)	600	(1)	410	420	0	2	36	230	13,000	190	0	500	3	13,000	7	200	35	20	100	0
150360	1	470	.1	1,100	350	6	0	55	150	11,000	430	0	700	3	7,500	12	140	38	0	100	0
150359	(1)	4,600	(1)	620	800	3	3	95	1,800	22,000	750	6	2,200	5	3,000	11	1,500	160	20	400	10
150355	(1)	1,200	(1)	1,600	570	0	2	65	740	19,000	320	5	1,100	3	12,000	15	300	72	20	400	10
150349	(1)	4,700	(1)	1,400	140	0	18	11	2,800	4,500	130	0	2,300	5	4,100	7	200	650	0	0	90
150347	.4	2,200	(1)	250	70	0	11	27	2,200	9,200	80	5	4,400	3	10,000	11	180	1,200	20	400	230
58-375	0	1,000	.4	190	360	0	3	19	1,000	11,000	80	0	1,500	35	6,800	11	120	100	10	200	10
		1,000	.4	140	950	0	2	62	580	6,000	65	0	1,000	3	10,000	23	270	110	10	0	20

1 Insufficient quantity of sample for analysis.

2 Mineral matter.

3 Species was not determined.

A12 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

Food and Drug Administration personnel rechecked the *Vaccinium canadense* sample and found 86 ppm lead in the dry weight using a gravimetric method.

TABLE 3.—Average and maximum trace element contents in ash of *Equisetum*, in parts per million, compared with the average for all types of vegetation

Element	Average content expected in all types of vegetation ¹	Average content of eight samples of <i>Equisetum</i> from unmineralized ground	Maximum content in all samples of <i>Equisetum</i> that were analyzed	Metal produced in district where maximum content was found
Barium.....	1, 100	430	4, 500	Hg
Boron.....	580	570	1, 600	None
Chromium.....	13	< 5	18	None ²
Cobalt.....	≈ 7	≈ 2	30	Pb, Zn
Iron.....	7, 000	1, 180	15, 000	Pb, Zn
Gold.....	< 0. 1	0. 2	0. 5	Hg
Lead.....	70	12	420	Zn, Pb
Manganese.....	3, 300	250	29, 000	Mo
Molybdenum.....	13	< 5	150	Mo
Nickel.....	65	7	280	Mo
Silver.....	< 1	< 1	2	Au
Strontium.....	1, 730	300	1, 500	None
Titanium.....	460	280	1, 200	None ²
Vanadium.....	20	< 14	50	Mo
Zinc.....	1, 220	< 200	9, 000	Zn
Zirconium.....	20	< 50	230	None ²

¹ Calculated from published analyses and from data in U.S. Geol. Survey files.

² Beach sands.

TABLE 4.—Copper, lead, and zinc in plants growing in acidic sulfide environment of Ore Hill mine, New Hampshire, in parts per million

[Analysts: H. W. Lakin and L. E. Reichen]

Location and kinds of sample	Copper		Lead		Zinc	
	In dried plant or soil	In ash of plant	In dried plant or soil	In ash of plant	In dried plant or soil	In ash of plant
Rusty stream flowing past tailings dump, total heavy metal, 16 ppm, pH 3.5:						
Algae, <i>Spirogyra</i> type.....	920	1, 300	6, 600	9, 420	2, 900	4, 140
Edge of ore dump:						
Surface soil.....	120	-----	660	-----	390	-----
<i>Betula alba</i> , paper birch.....	13	37	23	65. 7	540	1, 540
<i>Pinus strobus</i> , white pine.....	12	25. 5	23	48. 9	100	210
Above dam:						
Surface soil.....	100	-----	660	-----	190	-----
<i>Betula alba</i> , paper birch.....	26	74. 2	9	25. 7	650	1, 850
<i>Vaccinium canadense</i> , blueberry (stunted, red coloration in foliage).....	19	55. 9	81	238	120	350
Outcrop of schistose hanging wall:						
<i>Equisetum arvense</i> , horsetail (chlorotic).....	20	80	90	360	1, 400	5, 600
Old pile of tailings:						
<i>Equisetum arvense</i> , horsetail (healthy).....	38	152	86	344	400	1, 840
Composite sample of tailings at depth of 4 ft ¹	2, 000	-----	21, 000	-----	27, 000	-----

¹ Analyzed by U.S. Bur. of Mines.

LEAD-ZINC DISTRICT OF SOUTHWESTERN WISCONSIN

A study of the element content of *Equisetum arvense* and *E. kan-sanum* that grew on substrates ranging from unmineralized to heavily mineralized was made in the lead-zinc mineral district of southwestern Wisconsin. Analyses of samples of the plants and of the soil or of evaporite from water in which the plants grew are given in table 5.

The amounts of the macronutrient elements calcium and magnesium are less variable in the plants than in the soil and evaporite (table 5). This fact may indicate that absorption of these elements by *Equisetum* is related to metabolic requirements of the plant. The amount of the micronutrient zinc that is absorbed is directly related to the amount in the soil, but only on soils having a low zinc content does the amount of zinc in plant ash exceed the amount in the soil. The range in amounts of this element in the plants, 100–8,000 ppm, indicates that absorption of zinc (at least in large amounts) is not controlled by metabolic requirements of the plant, and that *Equisetum* can be considered a zinc accumulator.

In contrast to the concentrations of zinc, the amounts of the micronutrient copper are the same in all *Equisetum* samples, in spite of the fourfold difference between the low and high values in the soils. The absorption of the micronutrient manganese is similar to that of copper, and a relation of the absorption of both elements to metabolic requirements is suggested.

The micronutrient iron appears to be absorbed in amounts greater than are required for metabolism, and these amounts are dependent in part on the amount in the soil. The greatest amount of iron in *Equisetum* reported in table 5, 15,000 ppm, was found in the ash of plants that grew on soil having 50,000 ppm iron.

The remaining elements listed in table 5 commonly are considered to be nonnutritive (Sutcliffe, 1962, p. 6) and in general are not concentrated in the plants in amounts greater than are in soils unless the soils contain a greater than normal concentration of the elements. This tendency in concentration is illustrated by the amounts of cobalt, lead, nickel, and titanium in both soil and plant samples at the heavily contaminated New Diggings site; however, chromium, vanadium, and zirconium do not have this relationship in the two kinds of samples.

Although *Equisetum* may accumulate large amounts of zinc and lead if growing in metal-rich soils, some other plants at the New Diggings site contained even larger amounts of these elements. For example, ragweed (*Ambrosia artemisiifolia* L.) contained 12,000 ppm zinc and 500 ppm lead in its ash. Redcedar (*Juniperus virginiana* L.) stems and leaves contained 80 ppm copper in the ash—an amount four

TABLE 5.—Amounts of certain elements in the ash of Equisetum and in soils and evaporite at selected mineralized and unmineralized sites in southwestern Wisconsin

[Analysts: Maurice DeValliere, J. C. Hamilton, Margaret Hinkle, John McHugh, H. M. Nakagawa, and J. H. Turner. >, greater than the stated value; <, less than the stated value; nd, not detected; --, soils were not ashed]

Location and kind of sample	Laboratory No.	Ash content (percent)	Elements, parts per million																	
			B	Ba	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sr	Ti	V	Zn	Zr		
Fotosi, Grant County ¹																				
Soil in pool at spring	D0004468	---	15	200	95,000	5	30	7	5,000	20,000	700	10	100	70	1,000	20	700	150		
<i>Equisetum arvense</i>	D0003006	34	nd	100	70,000	nd	7	20	1,500	30,000	100	nd	<25	100	100	nd	200	nd		
Ipswich, Grant County ²																				
Soil, B horizon	D0004543	---	30	700	6,000	7	70	15	15,000	3,000	700	15	10	150	3,000	50	50	300		
<i>Equisetum kansanum</i>	D0003200	36	150	150	50,000	nd	nd	20	700	10,000	200	15	<25	300	30	nd	100	nd		
Tennysen, Grant County ³																				
Evaporite	D40275	---	10	<100	150,000	<10	40	10	<500	50,000	50	10	10	<500	<20	<20	1,250	<50		
<i>Equisetum arvense</i>	D0003935	34	70	150	140,000	nd	nd	20	1,500	50,000	100	nd	25	200	50	nd	50	800		
New Diggings, Lafayette County ⁴																				
Soil, A horizon	D0004563	---	20	200	94,000	20	10	30	50,000	10,000	700	30	1,000	100	700	5	40,000	100		
<i>Equisetum arvense</i>	D0003500	35	70	>100,000	30	10	20	15,000	30,000	1,000	1,000	100	150	150	300	nd	8,000	30		

¹ Spring issuing from dolomite in a mineral district, but no known mineral deposits at the site.

² Relict prairie with residual soil 6 ft thick to dolomite; no known mineral deposits at the site.

³ Spring issuing from dolomite, at base of hill on which a lead-zinc mine is located; no known surface contamination.

⁴ Abandoned mine and mill; soil heavily contaminated with lead and zinc ores.

times greater than the maximum copper content of *Equisetum* at this location.

Both gold and silver were looked for by means of semiquantitative spectrographic analysis, but neither element was found in these *Equisetum* samples.

VARIOUS PARTS OF ALASKA

Samples of four species of *Equisetum* were collected in Alaska from three mining districts and one area where there are no known ore deposits (table 6). The McGrath sites are in deposits of sandy alluvium adjacent to the Kuskokwim River. There are no known ore deposits in the vicinity of these sites; however, the Kuskokwim River and its tributaries drain areas of known mineral deposits. The metal values for *Equisetum* from McGrath, therefore, may not represent background values for this plant.

The Red Devil sites were in areas where quicksilver ore (cinnabar) was being, or had been, mined. The minerals associated with the cinnabar deposits are stibnite, realgar, orpiment, and native mercury (Cady and others, 1955, p. 105–106). Mining operations or placer ore presumably had contaminated the sites, although the substrate of *Equisetum* was largely loess.

One Latouche Island site was near a copper mine and mill (now inoperative) and was heavily contaminated by leachings from a tailings pile and dust from the ore mill. Another site on this island was on the workings of a small prospect pit, and two sites were on the undisturbed muskeg; one was above a large pyrite body that was said by Stejer (1956, p. 114) to contain copper, lead, and zinc minerals, and the other was above graywacke that contained no known mineral deposits.

The Kantishna site, in the Alaska Range a few miles outside Mount McKinley National Park, is in a small drain from tailings of a gold mine (now inoperative) at a lode deposit. Gold, silver, lead, and antimony are the chief metals of economic value in this area, but pyrite and arsenopyrite are also common (Wells, 1933).

Analyses of the samples from McGrath suggest that the values are somewhat higher than those in the background samples, and the metals in the alluvium may have come from mineral deposits upstream. Both gold and silver were found in all samples. Because the three *Equisetum* species at this location grew in different types of habitat, these data do not conclusively demonstrate a difference in metal absorption between species—the differences that are shown may be due to variation in metal content of soils at the sites. The samples from Latouche Island and Kantishna were analyzed before the currently used sensitive method for gold determination was available, and the semiquantita-

TABLE 6.—*Accumulation of elements by Equisetum*

[Collector: Hansford T. Shacklette. Analysts: Harry Bastron, E. F. Cooley, Thelma Harms, D. Marx, C. S.

Locality	Element in the substrate in excess of background values	Sample No.	Species of <i>Equisetum</i>	Ash-content (percent)	Element ¹		
					Ag	Al	Au
McGrath:							
In muskeg over alluvial sand.....	None known	58-369	<i>limosum</i>	15.1	1	1,000	0.4
Do.....	None known	-370	<i>sylvaticum</i>	13.2	1	1,000	.2
Do.....	None known	-371	<i>arvense</i>	14.8	1	2,000	.4
Red Devil:							
In ravine by mercury smelter....	Hg, Sb, As	-372do.....	24.6	nd	1,000	.1
In lake fed by drain from abandoned mercury mine.	Hg, Sb, As	373	<i>limosum</i>	14.1	nd	2,000	.5
On loess near active mercury mine.	Hg, Sb, As	-374	<i>sylvaticum</i> ...	14.5	1	1,000	.4
Latouche Island:							
In muskeg over pyrite body.....	Fe, S, Cu	57-2982	<i>pratense</i>	12	<2	-----	-----
In muskeg over graywacke.....	None known	-2997do.....	21	<2	-----	-----
In drain from Beatson copper mine tailings.	Cu, S	-3128do.....	15	Tr.	-----	-----
Slate dump by prospect pit near Duke mine.	Fe, S	-3135do.....	18	<2	-----	-----
Kantishna: In drain from tailings, Red Top mine.	Au	-3784	<i>sylvaticum</i> ...	32	2	-----	-----

¹ Looked for but not found: As, Be, Bi, Cd, Ce, Ga, Ge, Hf, Hg, In, Ir, La, Li, Nb, Pd, Pt, Re, Ru, Sb,

tive spectrographic method did not detect gold in these samples, although silver was found in two of them.

The values presented in table 6 show that analyses of *Equisetum* tend to correspond with the presence of large amounts of certain metals in the substrate. This tendency is illustrated by the relatively large amounts of copper, lead, nickel, and zinc in ash of the plants from the prospect pit at Latouche Island and from the mine tailings on this island and at the Kantishna site. Other kinds of plants, however, are equally useful for biogeochemical prospecting at similar sites.

SUMMARY OF THE CONCENTRATION OF TRACE ELEMENTS IN EQUISETUM

ZINC

The zinc content of the ash of *Equisetum* growing on unmineralized ground is less than 200 ppm, which is considerably lower than that in average vegetation. The plant can, however, accumulate large amounts of zinc when the zinc is in a soluble form. The maximum amount accumulated was 9,000 ppm from the Friedensville slime ponds.

The collections from the drained and undrained mucks near Manning, N. Y., which receive lead and zinc from the mineralized Lockport Dolomite, illustrate differences in uptake. The largest amounts of copper, lead, zinc, manganese, iron, strontium, and barium were absorbed from the drained oxidized muck. The least amounts, regardless of soil contents, were absorbed from the bogs in which the metal has remained in a reduced state (table 7).

species from Alaska, in parts per million of ash

Papp, and G. H. VanSickle. nd, not detected; <, less than the amount stated; Tr, trace; ..., no data available

Element 1—Continued																	
B	Ba	Co	Cr	Cu	Fe	Mg	Mo	Mn	Na	Ni	P	Pb	Sn	Ti	V	Zn	Zr
20	800	2	4	80	590	4,000	25	630	3,000	6	6,000	nd	nd	100	10	200	10
30	1,100	nd	2	39	340	8,000	7	230	1,000	5	5,000	nd	nd	84	nd	250	nd
40	750	nd	9	62	840	20,000	14	110	3,000	6	6,000	nd	nd	260	20	200	10
30	380	nd	5	35	330	30,000	nd	45	2,000	nd	4,000	nd	nd	64	10	100	nd
30	600	3	9	62	1,100	40,000	15	650	7,000	3	20,000	nd	nd	210	10	150	20
60	4,500	14	2	48	320	30,000	nd	700	3,000	21	6,000	nd	nd	64	10	250	nd
100	500	<10	<20	80	2,100	20,000	<10	3,000	-----	10	-----	100	<10	10	<10	400	<10
100	300	<10	<20	40	300	15,000	<10	150	-----	50	-----	100	<10	<10	<10	200	<10
200	500	10	<20	150	500	20,000	<10	500	-----	50	-----	200	<10	10	<10	2,000	<10
100	200	20	<20	100	200	20,000	<10	1,000	-----	200	-----	200	<10	10	<10	1,000	<10
100	30	<10	<20	80	3,000	20,000	<10	200	-----	5	-----	100	<10	50	<10	4,000	<10

Sc, Ta, Th, Tl, U, W, Y, and Yb.

After the mucks in an area south of Manning were drained, the availability of zinc in the peat increased and toxic areas developed where no crops could be grown (Cannon, 1955).

Large concentrations of zinc were also found in *Equisetum* growing in the Black Hawk gold district, Colorado, the Ore Hill lead-zinc mine in Warren, N.H. (table 4), the zinc mine at Franklin, N.J., the Wisconsin lead-zinc district (table 5), and Kantishna, Alaska (table 6).

LEAD

The amounts of lead absorbed by *Equisetum* in unmineralized areas averaged only 13 ppm in the ash. The extremely high values of 350 and 420 ppm found in *E. arvense* at the Ore Hill mine were not caused by traffic contamination and are valid, for the mine has been inactive for 25 years, and the collection sites are not near the highway.

TABLE 7.—Zinc and lead absorption by *Equisetum* growing on drained and undrained bogs near Manning, N.Y., in parts per million of ash

[Analyst: L. E. Reichen]

Location of sample site	Zinc		Lead	
	Plant	Soil	Plant	Soil
Undrained area near north edge of Oak Orchard bog.....	1,000	6,700	16	26
Drained and oxidized muck in same bog.....	1,300	2,100	83	12
Undrained bog south of Albion....	100	8,400	7	100

The absorption of lead, copper, and zinc by *Equisetum* as compared with other plants growing at Ore Hill, N.H., is shown in table 4. These primitive plants appear to accumulate more lead than trees or shrubs but not nearly as much as the algae growing in the stream that drained the tailings.

Fairly high values were obtained at the New Diggings site in Wisconsin, below the tailings of the Climax Molybdenum mill in Colorado, in drainage from the Black Cat gold mine at Black Hawk, Colo., and in the mineralized peat bogs near Manning, N.Y. All lead values were high in samples collected on Latouche Island and at Kantishna in Alaska.

COPPER

The average background copper content in different classes of vegetation ranged from 120 to 250 ppm in the ash. Background copper in samples of the ash of *Equisetum* averaged only 48 ppm.

Two samples of *Equisetum arvense* were collected at a copper mine in altered volcanic schists at Ely, Vt. One grew on tailings and contained 100 ppm copper; the other grew on natural soil near the mine shaft and contained 36 ppm. More copper was absorbed by *Equisetum* growing near a sulfide (copper-iron-uranium) ore body in a limbergite dike on Santa Fe Creek, N.Mex., than by that growing at Ely. High copper values were obtained in several samples collected near copper mines on Latouche Island, Alaska. The largest amount, 600 ppm in the ash, was found in *E. variegatum* growing in Black Canyon spring in the Gaddes Basalt near Jerome, Ariz. This basalt was not suspected to be an anomalous source of copper. Values of more than 100 ppm copper were found in *Equisetum* growing in mineralized areas that were economically valuable as sources of some other metal—for example, the Ore Hill lead-zinc mine at Warren, N.H.; the tailings of the Climax molybdenum mill, Colorado; the dump of a tungsten mine north of Nederland, Colo.; alluvium below the Black Cat gold mine at Black Hawk, Colo.; and the dump and stream alluvium below the Slick Rock uranium-vanadium mill in Colorado. The increased uptake of copper in some mineralized areas may be caused by the decrease in pH rather than by the total copper present in the soil. The *Equisetum* sample collected at the Kearsarge mine in Houghton, Mich., was found to be contaminated with mineral matter. This contaminant was separated from the ash and analyzed separately. Table 2 gives the results of analyses of the purified ash, the mineral contaminant, and an unrefined sample. The mineral matter contained nearly 2,000 ppm of copper, and the purified plant ash only 400 ppm.

GOLD AND SILVER

Gold in *Equisetum* throughout the conterminous United States ranged from less than 0.1 ppm in the ash to 0.4; the latter amount was in a sample collected as background material from Utley, Henderson County, Ky. Of the samples from mineralized areas, those collected in gold-producing districts averaged 0.17 ppm compared with 0.12 ppm in non-gold-producing areas. The samples collected in Alaska averaged 0.34 ppm; this value corresponds closely with those obtained by Warren and Delavault (1950) for Canadian samples. The difference in average content in plants growing on mineralized and unmineralized ground however, is not significant and suggests that *Equisetum* would not be useful in prospecting for gold.

Silver is absorbed by *Equisetum* more readily than gold, and the amount of silver absorbed seems to be related to the amount of silver present in the soil. Samples collected at the silver-producing Ore Hill mine, New Hampshire, averaged 1.4 ppm; those from other mineral districts averaged 0.7 ppm.

OTHER TRACE ELEMENTS

An anomalous amount of molybdenum was found in *Equisetum* from Climax, Colo., and also in that growing on mineralized limestone at Franklin, N.J. The uptake of molybdenum, unlike that of most metals, is favored by an alkaline environment.

Manganese, cobalt, nickel, chromium, vanadium, strontium, and boron contents were highest in the *Equisetum* collected at Climax. The titanium and zirconium contents suggest the possibility of dust contamination of the samples, although it is unlikely that the large amounts of other elements that were found can be attributed entirely to dust. The amounts of nickel found in *Equisetum* collected below the gold mine at Black Hawk, Colo., were high compared to those found at other sampling localities.

The concentrations of titanium, zirconium, and chromium in *Equisetum* samples that were collected as background material from beach sands along the eastern shore of Maryland may be significant for prospecting buried black-sand deposits. The concentration of these elements by the plants seems to be real and is not, as commonly suggested in the literature, purely a sign of dust contamination.

CONCLUSIONS

Twenty-two metals have been found in varying amounts in samples of *Equisetum* collected from areas mineralized with copper, lead, zinc, gold, tungsten, molybdenum, vanadium, uranium, and silver and also

from unmineralized ground. Contents of all metals are lower in the ash of background *Equisetum* than in average vegetation. The total metal content of *Equisetum* was generally lower than that of the ash of other plants growing in mineralized ground. Contents of lead, zinc, molybdenum, and silver were higher in *Equisetum* in districts where these metals were mined, but the contents of other metals were more closely related to availability than to total metal present. The accumulation of zinc in *Equisetum* from mineralized ground is greater than that of any other metal and is also large in comparison to the uptake of zinc by other plants. *Equisetum* can therefore be considered an accumulator of zinc.

No amounts of gold greater than 0.5 ppm were found in the ash of any sample. The samples collected from mineralized areas in Alaska had slightly higher gold contents than the samples collected in the conterminous United States. The high values reported in the early literature and since quoted by many writers may have been erroneous.

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the 1990s, the number of people in the UK who are employed in the public sector has increased from 10.5 million to 13.5 million, and the number of people in the private sector has increased from 18.5 million to 21.5 million (Department of Work and Pensions 2000).

There are a number of reasons why the public sector has grown so rapidly. One of the main reasons is that the public sector has become a major employer of people with disabilities. This is because the public sector is often seen as a more secure and stable employer than the private sector, and it is often seen as a more inclusive employer. This has led to a large number of people with disabilities being employed in the public sector, and this has led to a large number of people with disabilities being employed in the public sector.

Another reason why the public sector has grown so rapidly is that the public sector has become a major employer of people with mental health problems. This is because the public sector is often seen as a more secure and stable employer than the private sector, and it is often seen as a more inclusive employer. This has led to a large number of people with mental health problems being employed in the public sector, and this has led to a large number of people with mental health problems being employed in the public sector.

A third reason why the public sector has grown so rapidly is that the public sector has become a major employer of people with physical disabilities. This is because the public sector is often seen as a more secure and stable employer than the private sector, and it is often seen as a more inclusive employer. This has led to a large number of people with physical disabilities being employed in the public sector, and this has led to a large number of people with physical disabilities being employed in the public sector.

There are a number of reasons why the public sector has become a major employer of people with disabilities. One of the main reasons is that the public sector is often seen as a more secure and stable employer than the private sector, and it is often seen as a more inclusive employer. This has led to a large number of people with disabilities being employed in the public sector, and this has led to a large number of people with disabilities being employed in the public sector.

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