Biogeochemistry 2: 211–220 (1986)

Mercury-biogeochemical exploration for mineral deposits

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Key words: mercury, biogeochemical, prospecting, non-barrier, lithogeochemical

Abstract. Biogeochemical prospecting for mercury deposits and deposits of other minerals by the chemical analysis of mercury in plants or plant tissue that accumulate this element in linear (or near linear) proportion to the concentration in the soil is an effective method of exploration, even where allochthonous material as much as 200 to 2000 m thick covers the deposits. Plant tissues with this tendency to accumulate mercury (designated as non-barrier to mercury) comprise only a small fraction of the total of 255 types of plant tissues that were tested. Ten of these were considered to be quantitatively informative, and their mercury concentrations exceeded background values 300 or more times. The remaining types of plant tissues ranged in prospecting value from semi-quantitatively informative to qualitatively informative to uniformative (mercury values at or below background). The failure of some earlier uses of this prospecting method is attributed to the use of inappropriate plant tissues, to the mercury in the particular substrate studied existing in a form of low mobility and availability to plants, or to both causes.

Prospecting by examining mercury concentrations in soils and rocks (lithogeochemical prospecting) is more effective than the biogeochemical approach only in prospecting for cinnabar deposits having no allochthonous cover. Mercury-biogeochemical prospecting is most effective for non-mercury mineral deposits and for oil and gas deposits. The types of plant tissues used in these studies are listed and are classified according to their value in prospecting. A case history is given of the Ozernoe pyrite-polymetallic deposit in Siberia.

Introduction

The first attempt to use analyses of mercury concentrations in plants in exploring for mercury deposits was made in the USSR in the late 1940s (Epshtein 1948). Important data for the elaboration of this biogeochemical method were generated in Canada (Warren et al. 1966, 1983) and in the USSR (Bol'shakov et al. 1969; Malyuga et al. 1969; Znamirovskii 1971). Examination of these publications shows that mercury haloes revealed by plants were of low contrast in almost all examples given. These mercury values usually exceeded plant background values 2–8 times, thus these early data did not suggest the potential for the use of mercury in biogeochemical methods of prospecting. The low contrasts observed earlier can now be attributed to the unknown influence of two unfavorable factors acting singly or simultaneously; 1) the use of plant species and plant tissues that have low informative value in prospecting because they accumulate mercury up to some fixed limiting content (the so-called barrier types), because at that time the quantitiative barrier concept and prospecting characteristics of various types of plant tissues had not yet been studied; and 2) mercury in deposits of cinnabar is in a form unfavorable for uptake by plants.

Data obtained in the last several years demonstrate the effectiveness of mercury-biogeochemical methods by using nonbarrier plant species and plant tissues which accumulate mercury in direct and linear proportion to its concentration in mobile forms in the root-inhabiting zone of the substrate. This method is especially applicable in prospecting for non-mercury deposits, including oil and gas.

A brief discussion of methods of mineral prospecting by means of mercury determination in plants follows.

Prospecting informativeness of mercury in plants

Relationships of the mercury content of certain plant species and tissues of plants to high concentrations in soils were determined in 1977–1984 by studying their quantitative barrier characteristics (Anonymous 1983; Kovalevskii 1976, 1984). The 10 most informative types of tissues of the 255 that were investigated (Table 1) are as follows: trunk bark of 3 birch species (*Betula verrucosa*, *B. platyphylla*, and *B. pubescens*), outer trunk cork layers and needles of two larch species (*Larix dahurica* and *L. sibirica*), trunk middle cork layers of pine (*Pinus sylvestris*), haircap moss (*Polytrichum hyperboreum*), and a lichen (*Cladonia gracilis*). Most of the types of plant tissues (145 out of 255; 75%) have mercury concentrations exceeding local backgrounds 3–30 times (average, 10 times) and 96 out of 255 (38%) are of low information value, with concentrations ranging from background-barrier to 10 times background barrier and with a limited mercury content exceeding the background 2–5 times (average, 3 times). Fifteen types of plant tissues are non-responsive to high mercury concentrations in soils on the whole. This group includes bast (phloem fibers) or inner cork layers with bast, of tree trunks.

The statistical data of Table 1 demonstrates the predominance of barrier type plant tissues and emphasizes the necessity of using not just any, but only the small number, of nonbarrier and practically nonbarrier plant species and plant tissues in biogeochemical exploration using mercury as a pathfinder element.

Detection of various types of mineralization by mercury haloes in plants

Mercury-biogeochemical haloes in non-barrier plant tissues were revealed, without exception, by the investigations of 1977–1984 in all deposits and are occurrences that were studied of mercury, antimony, polymetals, gold, silver, copper, molybdenum, tungsten, beryllium, lithium, barium, boron, fluorine, manganese, and iron (Kovalevskii 1983, 1984; Kovalevskii and Radchenko 1983). As shown in table 2, the most contrasting mercury biogeochemical haloes with contrast coefficients (CC) up to 1200–5700 were established for mercury ore deposits having fine-grained and dispersed cinnabar. In non-mercury ore deposits, mercury biogeochemical halo CC's reached 30–130. The data in Table 2, and numerous publications (Fursov 1983; Hawkes 1982; Komov et al. 1982; Warren et al. 1983) confirm the widespread opinion that mercury is a universal indicator of various ore deposits. Taking into account the fact that mercury is a companion of various nonore deposits (Komov et al. 1982) and also oil and gas deposits (Fursov 1983; Ozerova 1982), it may be suggested that mercury is a biogeochemical indicator of a larger number of deposit types than those listed in Table 2.

Most mercury-biogeochemical haloes in non-mercury deposits coincide with, or are situated near, biogeochemical haloes of corresponding indicator elements in nonbarrier plant species and plant tissues according to the natural zoning (Kovalevskii 1983, 1984). Therefore, determination of 20–50 indicator elements in ash of plants from various mineral deposits gives important information for the interpretation of the biogeochemical anomalies and haloes that are found. Actually, mercury should be included in the list of the analyzed elements in all cases when, in biogeochemical prospecting for non-mercury deposits, plant species and plant tissues that are informative of high mercury concentrations (see Table 1) are sampled. In most situations plant ash should be analysed on the entire variety of readily determinable indicator elements when conducting biogeochemical exploration using mercury.

Comparison of mercury-biogeochemical, mercury-lithogeochemical, and gaseous-mercury methods

Comparable data on mercury-biogeochemical and mercury-lithogeochemical haloes were studied in 28 various ore deposits (Table 2). In most comparisons the degree of contrast of mercury-biogeochemical haloes in the non-barrier plant tissues was significantly higher than those of soil-geochemical ones. Only in cinnibar deposits and in the central part of the Zmeinogorskoe iron ore occurrence was the contrast of lithogeochemical haloes higher than biogeochemical ones. Similar correlations were established in Canada (Warren et al. 1966, 1983). Therefore, relations between contrasts of biogeochemical and lithogeochemical haloes given in Table 2 are rather typical.

The significantly greater degree of contrast (3–60 times) of biochemical haloes in mercury deposits compared to lithogeochemical ones in nonmercury ore deposits and in structure of hydrothermally altered rocks indicates that biogeochemical haloes are characteristic of the most mobile and,

Table 1. Grouping of Siberian plant tissues by their quantitative barrier and prospecting informativeness for mercury

Qualitative characteristics of plant tissue group	Plant tissues characteristics above intensive litho-geochemical mercury haloes[1]	Kind of plant tissues, in numbered sequence[2]	Number, and percent of total in shoots and roots, and sum of the two plant part numbers		
			Shoots	Roots	Sum
1. Nonbarrier, quantitatively informative, concentrating	$C_m > 1.5-15$ ppm and exceeding $C_b = 0.005-0.05$ ppm 300 times or more	1–10*	5 = 2%	0	5 = 2%
2. Hectabackground barrier, semi-quantitatively informative	$C_m = 0.5-5$ ppm and exceeding C_b 30–300 times	1–10* 11–38 39–70*	30.5 = 13%	18.5 = 71%	49 = 19%
3. Decabackground barrier, qualitatively informative	$C_m = 0.05-0.5$ ppm and exceeding C_b 3–30 times	39–70* 71–160 161–240*	138.5 = 61%	7.5 = 29%	146 = 57%
4. Background barrier, uninformative, nonconcentrating	$C_m < C_a$	161–240* 241–255	55 = 24%	0	55 = 22%

Explanation: *Plant tissues transitional between two groups.

[1] C_m, maximal; C_b, background; and C_a, minimal-anomalous mercury contents in the ash of corresponding plant tissues.

[2] Species of plant and plant tissue analyzed, as follows:

Group 1. 1–3 bark in lower trunk parts of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*; 4–7 needles and outer layers of trunk cork of *Larix dahurica*, *L. sibirica*; 8 middle cork layers of *Pinus sylvestris*; 9 *Polytrichum hyperboreum*; 10 *Cladonia gracilis*.

Group 2. 11–13 outer cork layers of *Pinus sibirica*, *P. silvestris*, *Picea obovata*; 14–15 middle cork layers of *Larix dahurica*, *L. sibirica*; 16–20 leaves of *Betula platyphylla* (65% of *Betula* species), *Ledum palustre*, *Dasiphora fruticosa*, *Rhododendron dahurica*, *Spiraea media*; 21–24 sprouts with needles or leaves of *Larix dahurica*, *L. sibirica*, *Dasiphora fruticosa*, *Rhododendron dahurica*; 25 suberized cones of *Pinus silvestris* from forest litter; 26–34 thick roots of *Betula verrucosa*, *B. pubescens*, *B. platyphylla*, *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. silvestris*, *Sorbus sibirica*, *Salix caprea*; 35–36 thick and thin roots of *Rhododendron dahurica*; 37–38 roots of *Ledum palustre*, *Spiraea media*; 39–40 middle cork layers of *Picea obovata*, *Pinus slbirica*; 41–43 inner cork layers of *Larix dahurica*, *L. sibirica*, *Pinus silvestris*; 44 trunk heart wood of *Pinus silvestris*; 45–49 leaves of *Betula humilis*, *Populus tremulus*, *Salix caprea*, *Salix* sp., *Vaccinium uliginosum*; 50–51 sprouts with leaves of *Ledum palustre*, *Spiraea media*; 52 twigs of Larix dahurica (46% of individuals); 53–54 suberized cones of *Larix dahurica*, *L. sibirica*; 55 forest litter of larch taiga; 56–64 thin roots of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. silvestris*, *Populus tremulus*, *Salix caprea*; 65–66 thick roots of *Picea obovata*, *Pinus pumila*; 67–70 shoots of *Astragalus melilotoides*, *A. membranaceus*, *Artemisia scoparia*, *A. frigida*.

Group 3. 71–72 outer and middle trunk cork layers of *Pinus pumila*; 73–74 inner trunk cork layers of *Picea obovata*, *Pinus sibirica*; 75–76 trunk cork of *Sorbus sibirica*, *Alnus fruticosa*; 77 bark of *Rhododendron dahurica*; 78–82 cork with bast of *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. silvestris*, *Pinea obovata*; 83–91 trunk heart wood of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. pumila*, *Picea obovata*, *Abies sibirica*; 92 sap wood of *Pinus silvestris*; 93–96 leaves or needles of *Betula verrucosa*, *Pinus silvestris*, *P. sibirica*, *Lonicera xylosteum*; 97–105 sprouts with leaves or needles of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *B. humilis*, *Pinus silvestris*, *Salix caprea*, *Salix* sp., *Populus tremulus*, *Vaccinium uliginosum*; 106–107 twigs or stems of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *B. humilis*, *Larix dahurica*, *Populus tremulus*, *Salix caprea*, *Salix* sp., *Ledum palustre*, *Vaccinium uliginosum*, *Dasiphora fruticosa*, *Spiraea media*; 118 upper stem parts of *Rhododendron dahurica*; 119–121 flowers of *Salix caprea*, *Rhododendron dahurica*, *Spiraea media*; 122–123 suberized cones from forest litter of *Pinus pumila*, *P. sibirica*; 124–126 bast of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*; 127–128 thin roots of *Picea obovata*, *Pinus pumila*; 129–145 shoots of *Leguminosae* (*Astragalus adsurgens*, *Vicia unijuga*, *V. sepium*, *V. cracca*, *Trifolium pratense*), *Vaccinium myrtillus*, *V. vitis-idaea*, *Calamagrostis epigeios*, *Sanguisorba officinalis*, *Paeonia anomala*, *Carex silvatica*, *Artemisia vulgaris*, *Pulsatilla tenuiloba*, *Arabis pendula*, *Silene venisa*, *Achillea asiatica*, *Equisetum sylvaticum*; 146–153 last year's remaining shoots of *Astragalus melilotoides*, *A. membranaceous*, *Calamagrostis epigeious*, *Artemisia scoparia*, *A. frigida*, *Arabis pendula*, *Silene venosa*, *Equisetum sylvaticum*; 154 *Boletus* sp. on birch bark; 155–160 Stump wood of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *Pinus silvestris*, *Larix dahurica*, *L. sibirica*; 161 trunk cork of *Populus tremulus*; 162 inner trunk cork layers of *Pinus pumila*; 163–167 cork with base of *Abies sibirica*, *Pinus pumila*, *Populus tremulus*, *Sorbus sibirica*, *Alnus fruticosa*; 168–177 sap wood of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *Larix dahurica*, *L. sibirica*, *Picea obovata*, *Abies sibirica*, *Pinus sibirica*, *P. pumila*, *Populus tremulus*; 178–181 wood of *Sorbus sibirica*, *Salix caprea*, *Alnus fruticosa*, *Rhododendron dahurica*; 182–188 leaves or needles of *Betula platyphylla* (35% of individuals), *B. pubescens*, *Pinus pumila*, *Picea obovata*, *Abies sibirica*, *Alnus fruticosa*; 189–201 sprouts of *Betula verrucosa*, *B. platyphylla*, *B. pubescens*, *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. silvestris*, *P. pumila*, *Picea obovata*, *Abies sibirica*, *Populus tremulus*, *Sorbus sibirica*, *Alnus fruticosa*; 202–211 twigs of stems of *Larix dahurica* (54% of individuals), *Pinus sibirica*, *P. silvestris*, *P. pumila*, *Picea obovata*, *Abies sibirica*, *Sorbus sibirica*, *Lonicera xylosteum*, *Alnus fruticosa*, *Rhododendron dahurica*; 212–214 lower, middle, and upper stem parts of *Alnus fruticosa*; 215–216 lower and middle stem parts of *Rhododendron dahurica*; 217–223 sprouts with leaves or needles of *Picea obovata*, *Abies sibrica*, *Pinus sibirica*, *P. pumila*, *Sorbus sibirica*, *Lonicera xylosteum*, *Alnus fruticosa*; 224–228 shoots of *Aconitum barbatum*, *A. Czekanovskyi*, *Epilobium angustifolium*, *Atragene sibirica*, *Allium ursinum*; 229–240 last year's remaining shoots of *Aconitum barbatum*, *A. Czekanovskyi*, *Astragalus adsurgens*, *Vicia unijuga*, *V. sepium*, *Epilobium angustifolium*, *Atragene sibirica*, *Sanguisorba officinalis*, *Paeonia anomala*, *Carex sylvatica*, *Artemisia vulgaris*, *Allium ursinum*.

Group 4. 241–242 cork and cork with bast in lower trunk parts of *Salix caprea*; 243–253 bast of *Larix dahurica*, *L. sibirica*, *Pinus sibirica*, *P. silvestris*, *P. pumila*, *Picea obovata*, *Abies sibirica*, *Populus tremulus*, *Sorbus sibirica*, *Salix caprea*, *Alnus fruticosa*, 254–255 shoots and roots of *Bergenia crassifolia*.

Table 2. Comparison of biogeochemical and lithogeochemical mercury haloes in ore deposits of Siberia

Types of deposits and ore occurrences	n[1]	Mercury contents, ppb		Contrast coefficient of haloes[2]
		Background[2]	Abnormal[2]	
Mercury	2	42–53 / 60–130	50000–300000 / 200000–20000000	1200–5700 / 3000–150000
Pyrite-polymetallic	2	20–33 / 30–70	800–4300 / 100–700	40–130 / 3–10
Fluorite-beryllium with pyrite	1	8–50 / 12–40	100–2500 / 60–160	5–120 / 3–8
Antimony	1	21–54 / 18–50	100–2200 / 100–300	5–110 / 3–10
Molybdenum	6	5–40 / 8–38	150–3300 / 20–150	30–80 / 2–4
Tungsten	2	9–16 / 14–19	180–940 / 30–120	20–60 / 2–6
Iron ore[3]	4	9–14 / 8–14 (20)	280–500 / 100–300 (2400)	30–50 / 12–36 (120)
Gold ore	9	11–38 / 14–31	240–800 / 30–150	8–44 / 2–5
Silver ore	1	7–30 / 14–70	100–500 / 100–480	5–36 / 3–14
Total or range	28	5–54 / 8–130	100–300000 / 20–20000000	5–5700 / 2–150000

[1] *n*, number of investigated objects.
[2] Numerator, in ash of nonbarrier plant tissues; denominator, in eluvial soil horizons at a depth of 1–5 m.
[3] Values in brackets for soil refer to Zmeinogorskoe iron ore occurrences, which differ significantly from other deposits in correlation of mercury in soils and plants.

for plants, the most readily available forms including gaseous mercury, the still poorly investigated organomercury, and other forms (Kovalevskii 1983, 1984).

Comparisons of biogeochemical mercury haloes with vaporous mercury haloes have given unexpected results. As shown in Table 3, in three deposits (two pyrite-polymetallic and one molybdenum) the degree of contrast (exceeding the local background) of the wide biogeochemical mercury haloes was significantly greater than that of local vaporous mercury haloes which presented an interchange of high concentrations and low near background values (Figure 1). This greater degree of contrast in biogeochemical haloes may be explained by the fact that the greater part (99–99.9%) of vaporous mercury is in the sorbed condition in the root-inhabited zone. The remaining insignificant quantity is very unstable, depending on a great number of factors of simultaneous influence (Stepanov 1983; Stepanov and Vil'dyaev 1984).

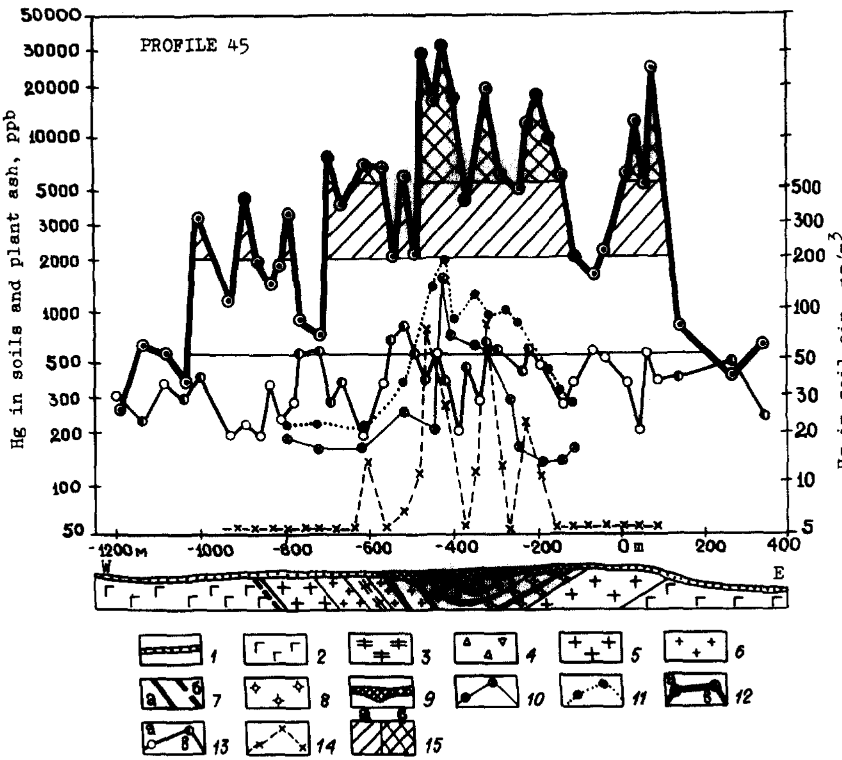

Figure 1. Mercury distribution in soils, plant ash, and soil air along profile 45 of the Ozernoe pyrite-polymetallic deposit (corrected for the mercury loss during plant sample ashing). Explanation. 1 – loose cover; 2–4 – Ozernoe series: 2, welded tuff horizon, lavas and welded tuff of andesite-dacite porphyrite with lenses and layers of limestone breccia and mineralized tuffites; 3, tuffite horizon, calcareous tuffites and breccia, tuff gritstone; 4, first productive horizon, limestones, limestone breccia and gritstone, tuffites, ignimbrite-type tuff and five orebodies; 5 – automagmatic breccia of rhyolite-dacite porphyry; 6 – dacite porphyry; 7 – pyrite-lead-zinc orebodies (a – prospected, b – suggested); 8 – sideritic ore; 9 – gossan of oxidation zone; 10–13 – mercury contents: 10, in soil horizon A (0–0.1 m); 11, in soil horizon C (0.5–1.2 m), 12 – comparable nonbarrier bio-objects: a, bark of *Betula platyphylla*; b, outer cork layers of *Larix dahurica*; 13, in background-barrier bio-objects: a, branches of *Betula platyphylla*, *Larix dahurica*, *Populus tremulus*, *Rhododendron dahurica*; b, sprouts of birch, larch, and aspen; 14 – in soil air (from data in IGO 'Buryatgeologiya'); 15 – biogeochemical anomalies of various intensity: a, average; b, high.

A comparison of the three geochemical methods shows that the lithogeochemical method is the most effective in prospecting for cinnabar deposits without allochthonous covers and that the biogeochemical method is the most effective for most non-mercury deposits. In choosing the principal geochemical method that uses mercury as an indicator of a specific type of deposit, it is necessary to comparatively evaluate the geological and economical effectiveness of all the alternative methods, including the mercury-biogeochemical one (Kovalevskii, 1981, 1982).

Table 3. Comparison of biogeochemical and atmogeochemical mercury haloes in pyrite-polymetallic and molybdenum deposits

Name of deposit and profile number	Kind of plant tissue, in numbered sequence[1]	Mercury contents				CC of haloes[3]	
		In plant ash, ppb		In soil air, ng/m^3		Biogeochemical	Atmogeochemical
		Background[2]	Anomalous	Background[2]	Anomalous		
Ozernoe, pyrite-polymetallic, profile 37	1, 2	$\frac{14-90}{33}$	200–4200	–	–	6–130	–
	3	$\frac{26-140}{50}$	250–2800	$\frac{7-19}{12}$	25–85	5–56	2–7
	4	$\frac{20-100}{40}$	320–3200	–	–	5–80	–
Ozernoe, profile 45	1, 2	$\frac{14-90}{33}$	200–3600	–	–	6–110	–
	3	$\frac{26-140}{50}$	250–1700	$\frac{7-19}{12}$	25–86	5–34	2–7
	4	$\frac{20-100}{40}$	320–1800	–	–	5–45	–
Nazarovskoe, pyrite-polymetallic, profiles 7.9, 8.1, 8.2	1, 2	$\frac{11-50}{20}$	100–800	–	–[4]	5–40	–
Malo-Oinogorskoe molybdenum, profile 1	1, 6	$\frac{12-70}{25}$	150–2000	–	–	6–80	–
	5	$\frac{19-100}{40}$	200–3000	$\frac{6-16}{10}$	20–85	5–75	2–8.5
Malo-Oinogorskoe, profile 2	1, 6	$\frac{12-70}{25}$	150–940	–	–	6–38	–
	5	$\frac{19-100}{40}$	200–1800	$\frac{6-16}{10}$	20–26	5–45	2–2.6

[1] 1, lower parts trunk cork of *Betula platyphylla*; 2, outer cork layers of *Larix dahurica*; 3, needles of *Larix sibirica*; 4, *Polytrichum commune*; 5, trunk cork of *Pinus sibirica*; 6, outer cork layers of *Larix sibirica*.
[2] Numerator, range; denominator, geometric mean.
[3] Contrast coefficient calculated as the relation of maximal concentrations to background.
[4] Mercury was not determined from soil water saturation.

Acknowledgement

The author acknowledges gratefully Dr H.T. Shacklette's assistance in correction and polishing the English text of this paper.

Conclusions and recommendations

1. Mercury-biogeochemical exploration is the method that is most informative in prospecting for deep mineral deposits and for geological mapping by the use of indicator elements in plats.
2. It is advisable to use this method mainly in prospecting for non-mercury deposits where the principal mercury forms in primary and secondary haloes are more mobile and available to plants than in cinnabar deposits with open outcrops of ore bodies.
3. It is also advisable to include the mercury-biogeochemical method in the complex of prospecting and structural geology studies in areas with overburden cover, including those where allochthonous cover reaches thicknesses of 200–2000 m.
4. Further investigations of the possibilities and advisability in practical use of the mercury-biogeochemical method in various geological and landscape conditions of the earth are necessary in the different known ore and non-ore mineral deposits, including deposits of oil and gas.

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