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DISTRIBUTION OF HEAVY METALS IN PLANTS AND THEIR HABITATS IN THE OUTCROP AREA OF DICTYONEMA SHALE

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The aim of the investigation was to find out the regularities of the concentration of heavy metals characteristic of Dictyonema shale in the mineral part of the roots of meadowsweet (Filipendula ulmaria), which is a well-known indicator plant. From 1996 to 2001 meadowsweet samples and soil samples around the roots were collected in 38 sampling points situated in the outcrop area of Dictyonema shale in Kunda–Aseri region. Root samples were washed, dried to constant weight and ashed at a temperature of 450 ºC. The soil samples were sieved, and the fraction <2 mm was used for the analyses. Cd, Cu, Fe, Pb and Zn soluble in aqua regia in ash and total concentrations of these elements in soil were analyzed by atomic absorbtion spectrometry; Mo and U were analyzed by X-ray fluorescence method.

Results indicate that Cu, Mo and Zn known as micronutrients or bioactive elements generally concentrate in the roots, and their content is close to the average one in the ash of plants. Some sampling points, however, show concentrations of these elements many times exceeding the average. Concentrations of "unfavorable" elements are different. The content of Pb in the ash of meadowsweet roots is close to the average, contrasting anomalies are lacking. Concentrations of Cd and U in ash are very heterogeneous, their averages are many times higher in plant ash, and they exceed the average dozens of times in some sampling points.

Although the soil does not seem to be influenced by anthropogenic pollution from the town of Rakvere and Kunda Cement Plant, the concentration of Cd, Cu and Pb in the ash of meadowsweet roots indicates the opposite. Analyses of the ash of meadowsweet roots reflect not only the high concentration of heavy metals in Dictyonema shale, but also their contrast concentration possibilities and anthropogenic pollution of the region.

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Introduction

The aim of the present study was biogeochemical investigation of the mineral part of the meadowsweet roots in plant habitats of Kunda–Aseri region (Fig. 1), which is one of the best-investigated areas of the North-Estonian Klint. In this region Dictyonema shale crops out in the middle of the klint escarpment. Dictyonema shale is rich in heavy metals (Cd, Cu, Mo, U, etc.). The fragments of Dictyonema shale crushed by continental glacier are distributed in the till of the klint zone, as well as in glaciolacustrine deposits and talus of the klint. On the map of the humus horizon of soil [20] the klint zone appears as a distinct belt with increased concentrations of heavy metals.

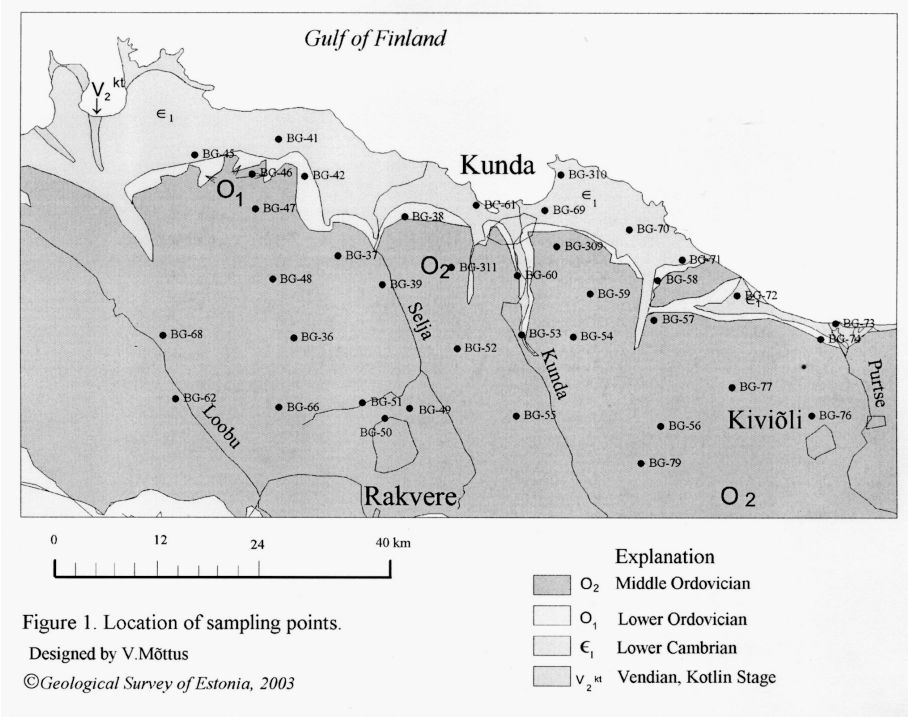


Fig. 1. Location of sampling points

Considering the experience of our Swedish colleagues [6], meadowsweet *(Filipendula ulmaria)* was selected as indicator plant. Meadowsweet is a perennial plant widespread in the klint zone as well as in whole Estonia in the lower parts of relief. Under favorable conditions the plants occur abundantly and grow (including their roots) luxuriantly.

Within the present study meadowsweet roots as well as soil samples to be analyzed were collected in the same sampling point. During summer-autumn seasons of 1996–2001 they were collected in 38 points.

All analyses were made at the Laboratory of the Geological Survey of Estonia accredited by the Estonian Accreditation Center on June 20, 2002 (certificate No. L093).

In the root and soil samples Cd, Cu, Fe, Pb and Zn were determined by AAS (atomic absorbtion spectrometry) and Mo and U by XRF (X-ray fluorescence) method.

Natural Conditions and Geological Setting

The elevation of the investigated area is up to 80 m above the sea level. Main relief elements are the limestone plateau, North-Estonian Klint, Fore-Klint Lowland and ancient valleys.

The limestone plateau spreads southward of the klint; its generally flat or undulating surface is cut by several ancient valleys (e.g. Toolse, Kunda) and open karst forms. The narrow (up to 15 km) Fore-Klint Lowland lies between the Gulf of Finland and the 10–50-m high klint escarpment.

Ancient valleys incise Palaeozoic bedrock to the depth of more than 60 m [9], but usually they are filled with Quaternary sediments being therefore difficult to observe in the present relief. Their width varies from some twenty or thirty meters to few kilometers.

Main rivers (Loobu, Selja, Pada and Kunda) begin south of the klint on the Pandivere Upland. In the Fore-Klint Lowland they meander, while on the limestone plateau, before the klint their beds form canyons which incise the bedrock to a depth of 20 m.

The investigated area is composed of three different rock complexes overlying each other: the Proterozoic crystalline basement, the Vendian and Palaeozoic sedimentary cover, and friable Quaternary sediments.

The crystalline basement rocks crop out about 20 km north, on the seabed of the Gulf of Finland. The crystalline basement is covered by a sequence of sedimentary rocks gently (about 3 m per km) dipping southward.

The Vendian sandstones and clays crop out in a very limited area within the ancient valleys in the Fore-Klint Lowland. They are overlain by the Lower Cambrian greenish-gray to variegated clay, silt- and sandstone, the Lower Ordovician Tremadock Obolus sandstone (phosphorite) and Dictyonema shale.

The phosphorite bed in the investigated area is 2.9 m thick [23], its main rock-forming minerals are quartz and biogenic phosphate represented by remnants of brachiopods. The content of phosphorus in detrital sandstone and conglomerate of different phosphorite deposits varies from 2–3 to 7–11%. In addition to phosphorus in the phosphate minerals, elevated concentration of Mo, U and other elements is observed; the latter occur as isomorphic addition [23].

Dictyonema shale is a fine-grained sedimentary rock rich in organic matter, potassium and pyrite. It crops out in the klint escarpment, forming 1.2–

3.4-m thick beds. Sand fraction accounts for less than 2% and is mostly composed of fragments of fossils [11]. A lot of microelements (Ag, As, Au, Cu, Mo, Sb, Tl, U, V) have been identified in Dictyonema shale, with concentrations which are 2–100 times, occasionally even more, in excess of the Clarke for clays [13, 21, 22]. The concentration of the elements increases to the east. In the central part of the area, in the shale overlying the phosphorite beds of Toolse deposit, the average concentration of U is 162 ppm and Mo – 406 ppm [19]; the concentrations of other elements (Cd, Cu, Pb, Zn and others) are elevated as well.

In the klint escarpment the Lower Ordovician Dictyonema shale is overlain by clay, glauconitic sandstone and glauconitic limestone, as well as limestone and dolostone. Outcrops of the Middle Ordovician limestone, marl and kukersite (oil shale) are situated south of the klint, on the limestone plateau. In the terrigenous and carbonate rocks of the area numerous polymetallic mineralization occurrences have been registered as well [20].

The thickness of the Quaternary sediments covering the bedrock is variable. Alvars (areas where the thickness of the Quaternary cover is less than 1 m) are quite common on the limestone plateau. Within the ancient valleys cutting into the bedrock the thickness of the Quaternary deposits is normally more than 20–50 m.

The Quaternary deposits in the observation area are represented mainly by till; in lower places of the relief the latter is often overlain by glaciolacustrine silts, sands and clays. To the north of the klint, on the Fore-Klint Lowland, the till is covered by sands and silts of different stages of the Baltic Sea, while contemporary marine deposits occur in the coastal zone. The ancient valleys are mostly filled with tills or glaciofluvial deposits. On about 10% of the area bog deposits (mainly peat) cover the terrigenous deposits. The debris in the tills is often represented by fragments of bedrock and crystalline basement, in which elevated concentrations of heavy metals occur, such as Dictyonema shale and phosphorite.

On the limestone plateau meadowsweet feeds mostly from subsoil water, in the Fore-Klint Lowland – from the subsoil water and groundwater drained from the klint.

Methods

Sampling

In sampling points meadowsweet roots and soil samples were collected. Sampling locations were selected considering the methods used in Sweden [6]: in upper courses of streams or drainage ditches, or in case of their absence, in hollows or depressions of the central lower parts of the relief. When streams were present, the samples were collected as close to the water table as possible. Samples were collected assuming that they characterize the drainage area of 3-5 km^2. Proceeding from the results of the Geological Sur-

vey of Sweden, it was presumed that in Estonia, too, the pollution with heavy metals in the sampling points reflects the pollution of the catchment area.

Collection of samples included describing the sampling point, distribution of indicator plants, humus horizon of soil and the underlying Quaternary deposits. The depth of the unconfined Quaternary aquifer was registered, too.

Meadowsweet root samples were carefully washed in stream water, and mechanical additions and decayed parts were removed. The weight of the samples was 1–1.5 kg of washed roots. The clean roots were dried and sent to the laboratory.

Soil samples were collected from the ground around the meadowsweet roots, trying to collect this sample as close to the roots as possible. Pebbles and plant roots were removed from the samples. The weight of the samples was 0.4–0.5 kg.

The meadowsweet roots and soil samples were collected in 38 sampling points (see Fig. 1).

Laboratory Processing

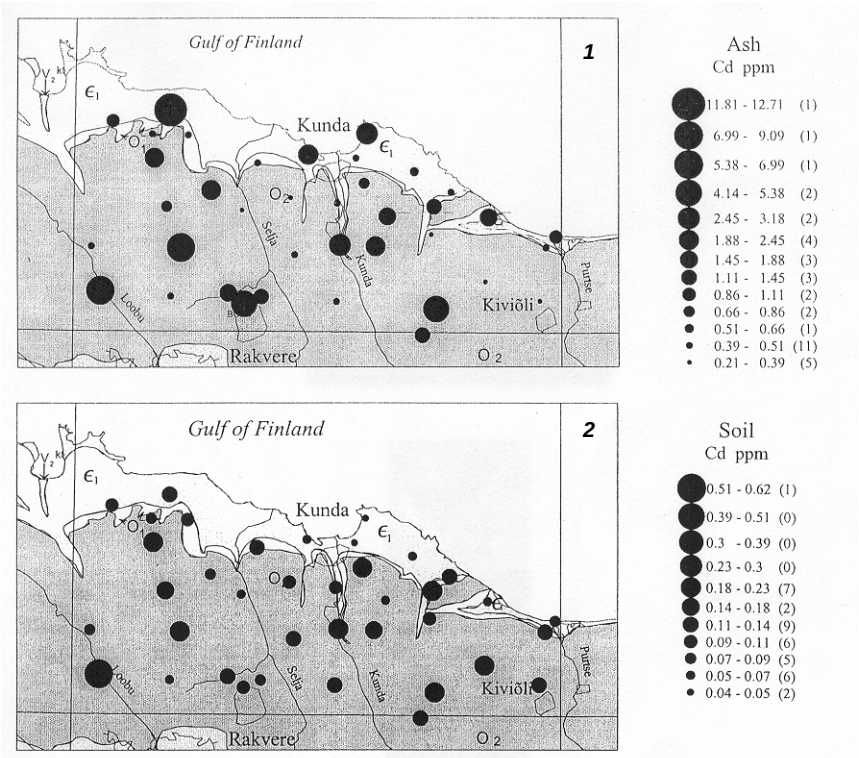
The root samples were cut to small pieces and dried to constant weight at 105 ºC. Ash content was determined after ashing the samples at 450 ºC. The content of Cd, Cu, Fe, Pb and Zn soluble in *aqua regia* in ash was determined by AAS, and that of Mo and U – by XRF method. The fraction <2 mm was separated from the soil samples and then analyzed. The same methods as for the meadowsweet root ash were applied for determining the elements in soil, but the total content of elements was determined. Detection limits of analyses were satisfactory, except for the concentrations of U which were often below detection limits (2 ppm).

The reliability of the laboratory data was checked using the reference samples of the former Ministry of Geology of the former Soviet Union as well as several international and local reference samples and by participating in intercalibration. The accuracy of the data meets the requirements posed to the analyses of the third category [5, 17, 18].

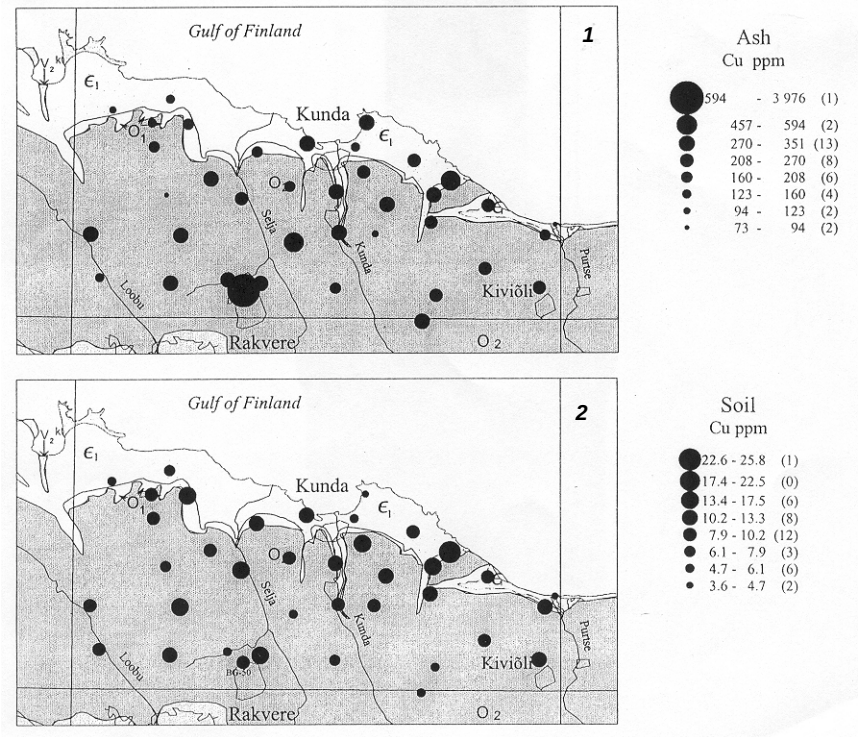
The figures characterizing the concentration and distribution of elements were compiled by computer program MapInfo Professional using the digital bedrock geological map of Estonia [24] (see Fig. 1). The size of the circle in the figures indicates the concentration of an element at a certain point (Fig. 2). The distribution regularities of elements were characterized using geometrical (log-normal) distribution. Using geometrical mean eliminates the influence of single high concentrations on the average value.

In calculations the U concentrations below the analysis detection limit were replaced by concentrations equal to half of the detection limit, i.e. 1 ppm. Therefore the calculated average concentrations are considered conventional ones.

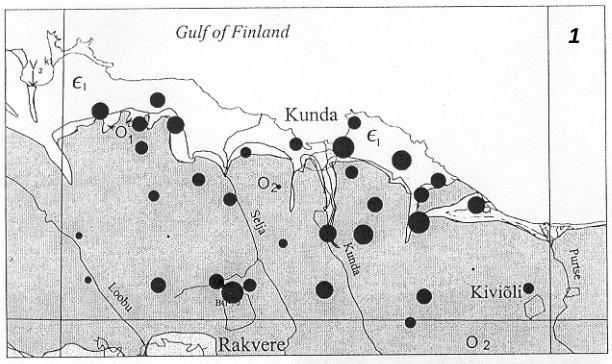
a

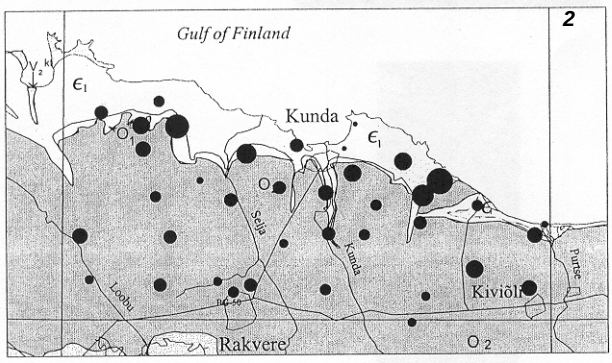

Gulf of Finland
1
Kunda
Sõja
Kunda
Purse
Loobu
Kiviõli
Rakvere
Ash
Cd ppm
11.81 - 12.71 (1)
6.99 - 9.09 (1)
5.38 - 6.99 (1)
4.14 - 5.38 (2)
2.45 - 3.18 (2)
1.88 - 2.45 (4)
1.45 - 1.88 (3)
1.11 - 1.45 (3)
0.86 - 1.11 (2)
0.66 - 0.86 (2)
0.51 - 0.66 (1)
0.39 - 0.51 (11)
0.21 - 0.39 (5)
Gulf of Finland
2
Kunda
Sõja
Kunda
Purse
Loobu
Kiviõli
Rakvere
Soil
Cd ppm
0.51 - 0.62 (1)
0.39 - 0.51 (0)
0.3 - 0.39 (0)
0.23 - 0.3 (0)
0.18 - 0.23 (7)
0.14 - 0.18 (2)
0.11 - 0.14 (9)
0.09 - 0.11 (6)
0.07 - 0.09 (5)
0.05 - 0.07 (6)
0.04 - 0.05 (2)

b

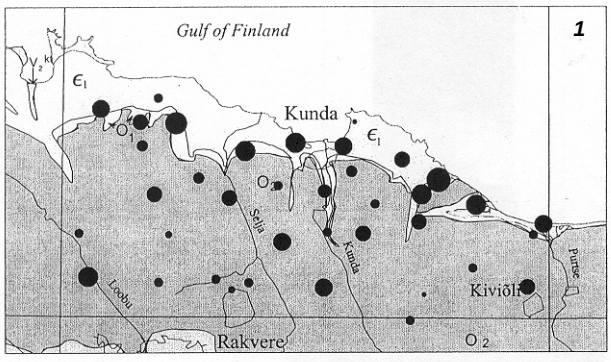

Gulf of Finland
1
Kunda
Sõja
Kunda
Purse
Loobu
Kiviõli
Rakvere
Ash
Cu ppm
594 - 3 976 (1)
457 - 594 (2)
270 - 351 (13)
208 - 270 (8)
160 - 208 (6)
123 - 160 (4)
94 - 123 (2)
73 - 94 (2)
Gulf of Finland
2
Kunda
Sõja
Kunda
Purse
Loobu
Kiviõli
Rakvere
Soil
Cu ppm
22.6 - 25.8 (1)
17.4 - 22.5 (0)
13.4 - 17.5 (6)
10.2 - 13.3 (8)
7.9 - 10.2 (12)
6.1 - 7.9 (3)
4.7 - 6.1 (6)
3.6 - 4.7 (2)

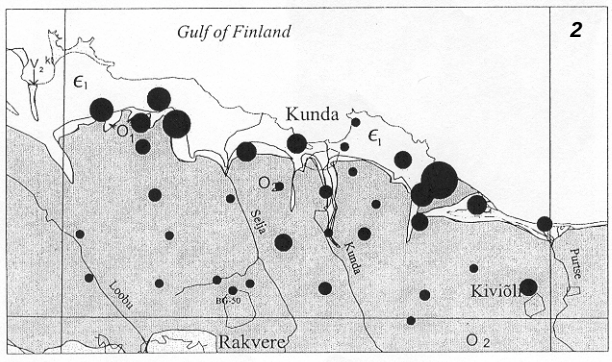
c


Gulf of Finland
1
Kunda
Selja
Kunda
Loobu
Kiviõli
Purse
Rakvere
Ash
Fe ppm
2.77 - 3.87 (3)
2.13 - 2.77 (2)
1.64 - 2.13 (5)
1.26 - 1.64 (8)
0.97 - 1.26 (7)
0.74 - 0.97 (4)
0.57 - 0.74 (1)
0.44 - 0.57 (2)
0.34 - 0.44 (1)
0.26 - 0.34 (5)

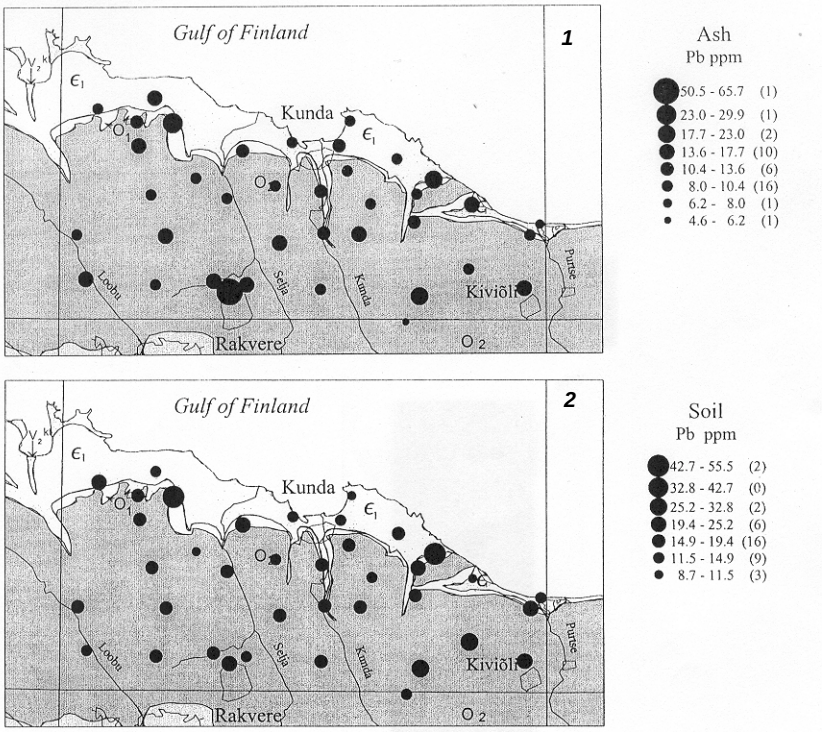

Gulf of Finland
2
Kunda
Selja
Kunda
Loobu
Kiviõli
Purse
Rakvere
Soil
Fe ppm
6.78 - 9.92 (1)
5.22 - 6.78 (1)
4.01 - 5.22 (1)
3.08 - 4.01 (1)
2.37 - 3.08 (4)
1.82 - 2.37 (5)
1.41 - 1.82 (9)
1.08 - 1.41 (7)
0.83 - 1.08 (5)
0.64 - 0.83 (2)
0.49 - 0.64 (2)

d

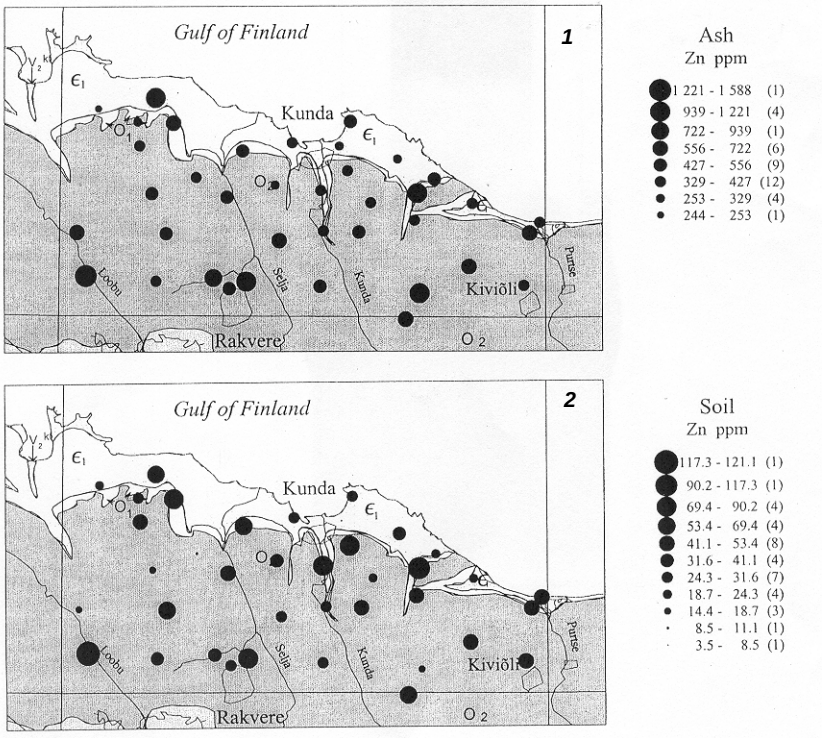

Gulf of Finland
1
Kunda
Selja
Kunda
Loobu
Kiviõli
Purse
Rakvere
Ash
Mo ppm
48.7 - 63.4 (1)
37.5 - 48.7 (1)
28.8 - 37.5 (5)
22.2 - 28.8 (5)
17.0 - 22.2 (7)
13.1 - 17.0 (1)
10.1 - 13.1 (3)
7.7 - 10.1 (11)
5.9 - 7.7 (2)
3.5 - 5.9 (2)


Gulf of Finland
2
Kunda
Selja
Kunda
Loobu
Kiviõli
Purse
Rakvere
Soil
Mo ppm
27.5 - 80.1 (1)
9.6 - 12.5 (1)
5.7 - 7.4 (3)
3.3 - 4.3 (4)
2.5 - 3.3 (4)
1.9 - 2.5 (2)
1.5 - 1.9 (4)
1.1 - 1.5 (1)
0.5 - 1.1 (16)

e


Gulf of Finland
1
Kunda
Loobu
Selja
Kunda
Kiviõli
Purtse
Rakvere
Ash
Pb ppm
50.5 - 65.7 (1)
23.0 - 29.9 (1)
17.7 - 23.0 (2)
13.6 - 17.7 (10)
10.4 - 13.6 (6)
8.0 - 10.4 (16)
6.2 - 8.0 (1)
4.6 - 6.2 (1)
Gulf of Finland
2
Kunda
Loobu
Selja
Kunda
Kiviõli
Purtse
Rakvere
Soil
Pb ppm
42.7 - 55.5 (2)
32.8 - 42.7 (0)
25.2 - 32.8 (2)
19.4 - 25.2 (6)
14.9 - 19.4 (16)
11.5 - 14.9 (9)
8.7 - 11.5 (3)

f


Gulf of Finland
1
Kunda
Loobu
Selja
Kunda
Kiviõli
Purtse
Rakvere
Ash
Zn ppm
1 221 - 1 588 (1)
939 - 1 221 (4)
722 - 939 (1)
556 - 722 (6)
427 - 556 (9)
329 - 427 (12)
253 - 329 (4)
244 - 253 (1)
Gulf of Finland
2
Kunda
Loobu
Selja
Kunda
Kiviõli
Purtse
Rakvere
Soil
Zn ppm
117.3 - 121.1 (1)
90.2 - 117.3 (1)
69.4 - 90.2 (4)
53.4 - 69.4 (4)
41.1 - 53.4 (8)
31.6 - 41.1 (4)
24.3 - 31.6 (7)
18.7 - 24.3 (4)
14.4 - 18.7 (3)
8.5 - 11.1 (1)
3.5 - 8.5 (1)

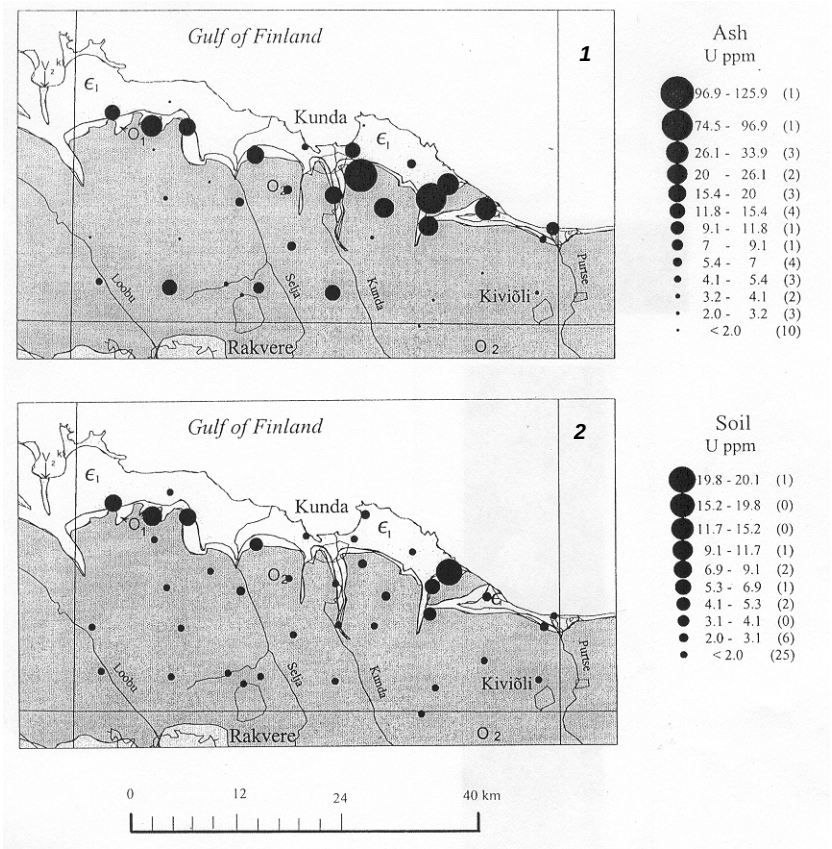


Fig. 2. Distribution of elements in ash (*1*) and soil (*2*) for: *a* – Cd; *b* – Cu; *c* – Fe; *d* – Mo; *e* – Pb; *f* – Zn; and *g* – U. In brackets the number of respective sampling points (designed by V. Mõtus)

Results and Discussion

The main object of the present study was to investigate the mineral part of meadowsweet roots which was obtained by ashing them at a low temperature (450 ºC) (further referred to as ash). The ash content of root samples is rather stable varying from 5.5 to 8.8% [5].

Cu, Mo and Zn concentrate in the mineral part of plants [3, 14]. Their background concentrations in soil favor growth and development of plants, and they are known as bioactive or micronutrients. The deficiency or excess of these elements may cause serious plant diseases. High concentrations of these elements in food are toxic.

Usually the concentrations of Cd, Pb and U in the mineral part of plants are lower than in soil [3, 14]. The influence of background concentrations of these elements on plants is not unambiguously identified, but they certainly have some positive function formed during the long evolution period. High

concentrations of Cd, Pb and U in food are partly toxic [7, 8]. Compounds of U are also carcinogenic and mutagenic [15]. These elements are known as unfavorable to the environment.

Fe is a soil-forming macroelement. With Fe background concentrations, soil is a neutral environment for plant habitats, with high concentrations – unfavorable one. Fe has also another function: Fe compounds are often carriers or concentrators of many heavy metals. This is observed in the soil of the study area, too.

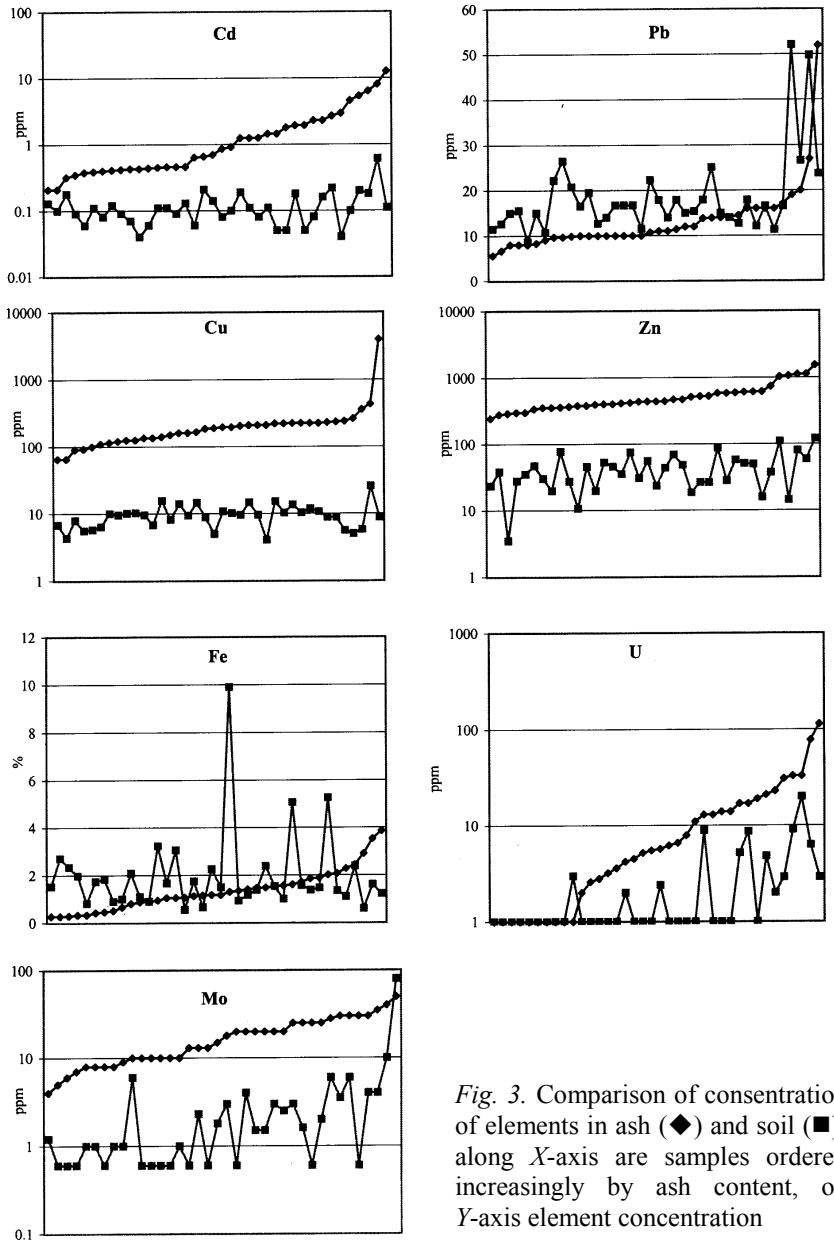


Fig. 3. Comparison of consentration of elements in ash (◆) and soil (■); along *X*-axis are samples ordered increasingly by ash content, on *Y*-axis element concentration

Cd concentration in plants varies and depends strongly on the pH of the soil. In the soil with background concentrations, the concentrations of Cd should range between 0.005–0.05 ppm [7] in the mineral material and 0.24 ppm in the ash of meadowsweet roots on an average.

Cd concentration in soil varies (see Fig. 2). On the one hand it is caused by variations in Cd concentration of Dictyonema shale (0.2–6.1 ppm), on the other hand by additional Cd from polymetallic mineralization. On this background Cd concentrated in ash and its concentration coefficient (the ratio of concentrations in ash and in soil) differ considerably – 0.21–12.70 ppm and 2–115, respectively. Special attention should be paid to the high Cd concentration in sampling points BG-50 and BG-310 (see Fig. 1). Point BG-50 is located on the bottom of a ditch which begins in the town of Rakvere, and the elevated Cd concentration is likely due to anthropogenic pollution from the town. Sampling point BG-310 is located about 3 km to the northeast of Kunda Cement Plant, in the central part of the most intensive smoke fan. In this region annually >0.16 ppb/m^2 of Cd precipitates from the atmosphere to the ground surface, about 60% of which is dissolved in rainwater [20]. The high Cd concentration in the nearby point BG-61 is also very likely caused by the pollution from Kunda Cement Plant.

The average Cd concentration in ash is about ten times higher than in soil and several times exceeds the average concentration in plant ash reported by several authors (further referred to as average concentration in plants) [3, 14] (Figs 2 and 3). It must be investigated more thoroughly whether such behavior of Cd is characteristic of meadowsweet roots only or of other plants, first of all cereals, as well. Such studies are especially important because high Cd concentrations were found in the ash of the meadowsweet roots while the concentration in the surrounding soil was low.

Cd concentrations in ash and soil do not show any correlation (Fig. 4).

Cu concentrations in dry matter of plants vary between 1–50 ppm [1]; average concentration in ash reported by different authors is 180 or 200 ppm [3, 14].

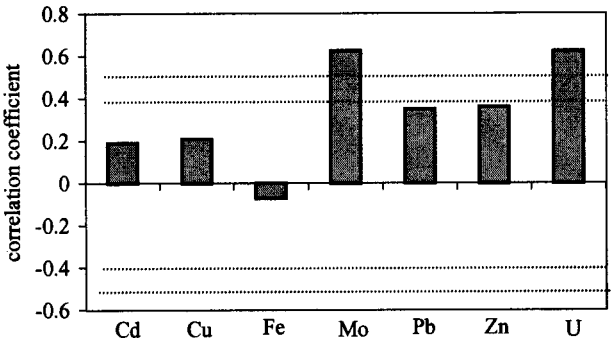


Fig. 4. Correlation between ash and soil according to their content of elements; distinct and significant correlation is 0.39 and 0.49, respectively

Average Concentrations (ppm, Fe – %) of Elements in Plant Ash (C_{ash}) and Soil (C_{soil}) of 38 Samples, Standard Deviations (SD) and Concentration Coefficients (C_{ash}/C_{soil}) as Compared with Corresponding Data of the Humus Horizon of Estonian Soil and Toolse Dictyonema Shale

Element	C_{ash}		C_{soil}		C_{ash}/C_{soil}	Humus horizon of Estonian soil [20]	Toolse Dictyonema shale [19]
	Average	SD	Average	SD			
Cd	0.99	3.02	0.10	1.73	9.9		1.6
Cu	183	1.94	9	1.50	20.3	14	75
Fe	1.09	2.00	1.60	1.81	0.7	1.41	
Mo	15	1.86	1.73	2.91	8.8	1.3	406
Pb	12	1.49	17	1.44	0.7	16.4	120
Zn	488	1.54	36	1.96	13.5	36	170
U	5.7	3.92	1.70	2.33	3.4	1.87	162

Concentration of Cu in the soil of the study area is close to the Estonian average (14 ppm) [20], and the dispersion is normal (Fig. 2; Table). The increased concentration of Cu occurs in Dictyonema shale [12], but in the surrounding soil Cu is hard to detect. On such low background the concentration of Cu in meadowsweet roots is about 20 times higher than in soil and varies, except for one point, between 65 and 435 ppm. This one very high concentration of Cu (3975 ppm) was observed in sampling point BG-50. Average concentration of Cu in ash is close to its average concentration in plants [3, 14]. The concentration coefficient of Cu differs as well and varies from 11 to 62.

High Cu concentration was found in point BG-50. It is obviously caused by anthropogenic pollution from the town of Rakvere.

Cu concentrations in ash do not follow the concentrations in soil (see Fig. 3), and there is no correlation between them (see Fig. 4). In single points the concentration of Cu in ash can several times exceed its respective average concentration in plant ash.

High concentrations of **Fe** are poisonous [10]. Fe is a bioactive element, and its role in regulating the metabolism of green plants is remarkable. In the soil of the study area the concentration of Fe in soil is close to the Estonian average (1.41%), and dispersion is quite large. The average concentration in ash is lower and the dispersion is lower, too (see the Table).

Fe concentrations in ash do not follow the concentrations in soil and there is no correlation between them (see Figs 3 and 4). Positive correlation is observed between Fe and some heavy metals in soil, which is not observed in ash.

Mo concentration in plants varies greatly, being mostly 0.17–2 ppm in dry matter [1]. In ash the average concentration is about 13 or 20 ppm [3, 14].

In the soil of the study area the concentration of Mo is close to the Estonian average (1.3 ppm), but dispersion is very high (see Figs 2 and 3, and the

Table). On the one hand it is caused by pieces or weathering products of Dictyonema shale in the soil, and on the other hand by very uneven distribution of Mo in Dictyonema shale itself [12]. On this background concentrated Mo values in meadowsweet roots vary considerably (4–50 ppm), but the average concentration is significantly higher and dispersion is lower than in soil (see Fig. 2, and the Table). The average concentration in ash is 8.8 times higher than the soil's average and is close to the average concentration in plant ash (see the Table).

Excluding some exceptional samples, the concentration of Mo in ash follows the concentration in soil, but on a higher level (see Fig. 3), consequently, there is a positive correlation between them (see Fig. 4). The concentration of Mo in the mineral part of plants may several times exceed its concentration in soil.

Pb concentrations in dry matter of plants vary between 0.1–20 ppm [1]. In the ash the average concentration is about 10 ppm [14].

In the soil of the study area the concentration of Pb is close to the Estonian average (16.4 ppm), and the dispersion is low (see Fig. 2, and the Table). Increased but uneven concentrations of Pb [12] in Dictyonema shale are revealed in the soil near its outcrop area (see Fig. 2). On this background the Pb concentration in ash varies between 6.7 and 20 ppm. The average Pb concentration in ash is about 25% lower than in soil and is also less than its average concentration in plant ash (see Fig. 3, and the Table). The concentration coefficient in samples is similar, mostly <1, and the dispersion is low. Only in the point BG-50 the concentration is remarkably higher (52 ppm). As mentioned before, this is probably due to the anthropogenic pollution from the town of Rakvere.

Pb concentrations in ash are mostly related to the concentrations in soil (see Fig. 3). Higher concentrations in ash correspond to higher concentrations in soil, which results in positive correlation (see Fig. 4). Depending on the concentrations in the soil, the concentrations in ash may increase several times above the average.

Zn concentration in dry matter of plants varies between 1.2 and 73 ppm [8]; different authors report average concentrations in plant ash ranging from 900 to 1500 ppm [3, 14].

In the soil of the study area Zn concentration is close to the Estonian average (36 ppm), and dispersion is elevated (see Figs 2 and 3, and the Table). Zn concentration in Dictyonema shale is usually increased but variable, and its influence on soil is scarcely observable [12]. To some extent the concentration of Zn in soil is influenced also by polymetallic mineralization in the carbonate bedrock. On this background Zn concentrations in ash vary between 244 and 1125 ppm, and the concentration in ash is about 14 times higher than in soil, but significantly lower than average concentration in plant ash (see Fig. 3, and the Table). The concentration coefficient in the samples is similar; it is high only in few samples where concentrations in

soil are very low (BG-37, BG-56, BG-69). It is probable that Zn accumulates in meadowsweet roots even when the surrounding soil is poor in Zn.

The concentration of Zn in ash in most cases follows the concentrations in soil (see Fig. 3), but on a higher level, and there is positive correlation between them (see Fig. 4). In few samples the concentration in ash may exceed the average several times.

High concentrations of **U** are the main sources of Rn [15]. Its concentration in dry matter varies from 5 to 69 ppb, average being 38 ppb [2]. Recalculation of these concentrations to the concentrations in mineral part of plants leads to an average of 0.6 ppm. It is known that around the factory of phosphorus fertilizers the content of U in ash of plants rises to 8 ppm [10].

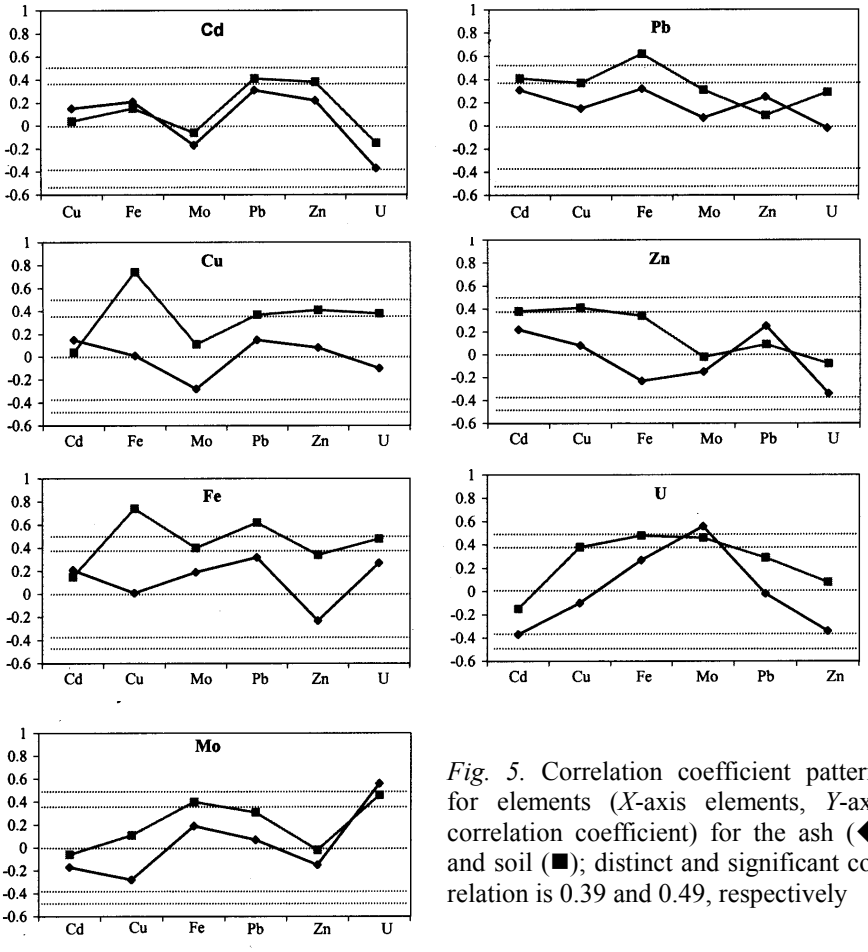


Fig. 5. Correlation coefficient patterns for elements (*X*-axis elements, *Y*-axis correlation coefficient) for the ash (◆) and soil (■); distinct and significant correlation is 0.39 and 0.49, respectively

In the soil of the study area the conventional concentration of U is close to the Estonian average (1.87 ppm), but concentrations variable and exceeding the detection limit occur only in klint zone (see Fig. 2). In the southern part of the area (on limestone plateau) the concentrations in general do not

exceed the detection limit (<2 ppm). Such distribution is caused by the decreased content of Dictyonema shale fragments or its weathering products and phosphorite south of the klint, as well as very uneven distribution of U in Dictyonema shale [12]. On the described background the U concentration in ash varies from less than 2 ppm up to 114 ppm. Average concentration and dispersion are much higher than in soil (see Figs 2 and 3, and the Table). However, the concentration coefficients of single sampling points are quite similar.

Excluding some exceptional samples, the concentration in ash follows the concentration in soil, but on a higher level (see Fig. 3), with a resulting positive correlation (see Fig. 4). U concentration in ash may even dozens of times exceed the average concentration in plant ash.

As mentioned before, the Dictyonema shale is rich in many heavy metals. They form positive element associations such as Mo–U–Fe and Cd–Pb–Zn, which are obviously present in the soil (Fig. 5), and Cd–Pb–Zn (Fe–Cu) association characteristic of polymetallic mineralization. These positive associations are not reflected in the ash. In the ash the tendency of correlations between these elements remains the same, but a significant positive correlation appears only between concentrations of Mo and U (see Figs 4 and 5).

Relations between the concentrations in ash and in soil are different. Analyses indicate that there is a significant positive correlation between Mo and U in ash and in soil; the correlation between Pb and Zn is weak, and between Cd and Cu there is no correlation (see Fig. 5). The main reason for this is the above-mentioned anthropogenic pollution.

In the soil of the study area some sampling points show increased concentrations of elements characteristic of Dictyonema shale. These elements, especially Cd, Cu, Mo and U, concentrate in the mineral part of meadowsweet roots. In the ash the average concentration of these elements is many times higher than in soil and also higher than maximum concentration permissible for residential areas [16]. After recalculation of these concentrations for dry matter, they exceed many times also the maximum concentrations permissible for cereals [4]. It is obvious that further investigations are necessary to find out whether elements in soil characteristic of Dictyonema shale concentrate also in other plants, e.g. cereals. Since U is the most important source for Rn, this element needs special attention.

Conclusions

The results show that increased concentrations of heavy metals characteristic of Dictyonema shale may occur in different habitats. Cu, Mo and Zn, known as micronutrients or bioactive elements, concentrate in ash, and their concentration coefficient is close to the average in ash reported by other authors. At the same time, in some sampling points high concentrations of these ele-

ments were analyzed in soil, and the values in ash were many times higher than the average of the study area.

Concentrations of Cd, Pb and U known as "unfavorable" for environment are different in the studied area. Concentration of Pb in ash is lower than in soil but close to the average reported by other authors. Contrasting anomalies are not observed. Concentrations of Cd and U in ash are very varied; their average concentration in ash is many times higher than in the soil of the study area and also higher than the average in ash reported by other authors. Moreover, in single sampling points concentrations in ash exceed the average of the study area dozens of times.

Cd, Cu and Pb values in ash differ from the values found in soil, which is caused by anthropogenic pollution from the towns of Rakvere and Kunda.

Positive associations of Mo–U–Fe and Cd–Pb–Zn characteristic of Dictyonema shale have been established in soil, but not in the ash. The latter shows a positive correlation only between Mo and U.

The correlation between Mo and U in ash and soil is significant and that of Pb and Zn is distinct, while there is no correlation between Cd and Cu. This might be caused by additional anthropogenic pollution.

The results indicate that the composition of ash reflects not only the high concentrations of elements originating from the fragments of Dictyonema shale and phosphorite or its weathering products in soil, but also the ability of plants to concentrate the above elements, as well as the anthropogenic pollution in the area.

In the study area there are some sampling points where elevated concentrations of elements characteristic of Dictyonema shale and phosphorite are observed in soil. These elements, especially Cd, Cu, Mo and U, concentrate in the ash and exceed several times the average concentrations of the study area. When calculated to dry matter these concentrations exceed the maximum concentrations permissible for cereals.

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