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Migration of microelements in main types of Southeast Estonian soil

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This paper deals with the migration of Cu, F, Hg, Mn, P, Pb, Zn, U in brown and podzol soil profiles of Southeast Estonia. The aim of the study was to find out why the soils in Southeast Estonia are poor in almost all elements – whether they are carried out from the humus horizon or the parent material of soil is initially poor in them.

The mean contents of the elements studied are 1.2–1.7 times lower as compared with Estonian mean contents; only Hg has a mean content similar to the Estonian mean. To solve this problem, the contents of the above-mentioned microelements were analysed in the humus horizon and parent material in brown and all podzol soils.

Analysis of the migration of elements shows that Cu, Mn, P, Pb, Zn are relatively sedentary in soil profile. The content of F and U in the humus horizon is twice lower than in parent material, while Hg content in the humus horizon is twice as high. Briefly: the main reason for the lack of nutrient microelements in brown and podzol soils in Southeast Estonia is their low content in parent material; carrying out from the humus horizon is less important.

Key words: soil geochemistry, migration of microelements, nutrient elements, hazardous elements

INTRODUCTION

This paper discusses the migration of some microelements (Cu, F, Hg, Mn, P, Pb, Zn, U) in brown and all podzol soil profiles of Southeast Estonia (Fig. 1).

The aim was to find out which microelements and in which amounts are carried out from the humus horizon and to explain the reason why the soils in Southeast Estonia are poor in almost all elements. As compared with the Estonian mean content of the elements, the mean contents of Cu and Pb are 1.2 times lower, Mn 1.6–1.7 times, F, P, Zn 1.4 times, U 1.3 times lower, and only the average content of Hg is similar to the Estonian mean (Petersell et al., 1997; Täht, Mõttus, 1998). The question is whether the microelements are carried out of the parent material or the soil is initially poor in them.

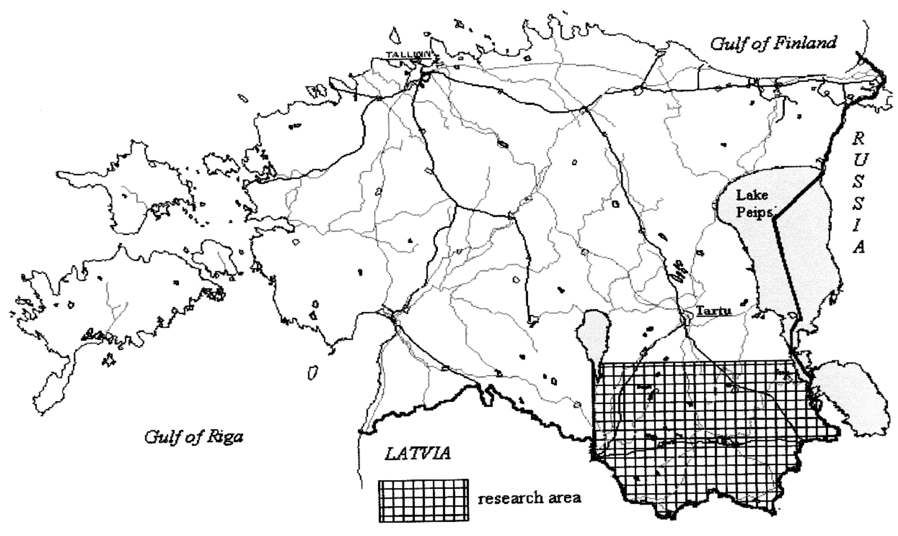

Fig. 1. Location of the research area

To solve this problem, the contents of the above-mentioned microelements were analysed in the humus horizon and parent material of the soil. In the present paper, the humus horizon of soil constitutes the upper layer of the soil profile containing humified organic matter (OM). The OM content in it is normally <5% and the total OM exceeds 10–15% only in exceptional cases. OM-rich peat-based soils (OM >50%) have been excluded. Parent material of the soil is the horizon that has not been affected by soil-forming processes. Excluded were all gley soils, because the humus horizon in them can be enriched with microelements occurring in groundwater. The aim of the study was to examine natural processes in brown and all podzol soils, therefore abnormal and obviously polluted soils were not considered.

The parent material of the soil in Southeast Estonia has been formed of thick Quaternary sediments. In the hills and buried valleys their thickness reaches 50–200 m. The Quaternary cover consists mainly of till, glaciolacustrine and glaciofluvial deposits, while alluvial and aeolian deposits are less common. The till is mainly loamy sand or sandy loam. Glaciolacustrine deposits are represented mainly by fine sand, silt and clay (Kajak, 1999).

In Southeast Estonia, different types of podzol soils prevail (Kask, 1996). Brown, pseudopodzolic, sod-podzolic and podzol soils are considered in the present paper. These are soils that are more or less drained by water.

Brown soils (K_{0+1}) (Kõlli et al., 1998) are formed mainly on tills or sometimes on glaciofluvial deposits and are mainly loamy clay soils. In these soils, carbonates leach out only from the humus horizon. Brown soils are fertile soils.

The main characteristic feature of pseudopodzolic soils (LP) (Kõlli et al., 1998) is that they are formed on two layers of parent material. Usually till sediments are covered with lighter ones, *e.g.*, sandy loam with loamy sand. Carbonates are leached out from eluviation (leaching out) and illuviation (washing in) horizons. Pseudopodzolic soils are also fertile soils.

Sod-podzolic soils (Lk) (Kõlli et al., 1998) are formed mainly on glaciolacustrine sandy sediments and are mostly loamy sand and sand soils. Sod-podzolic soils are poor in carbonates and clay particles, they are acid soils. Sod-podzolic soils often suffer from dryness and are not very fertile soils.

Podzol soils (L) (Kõlli et al., 1998) are formed on aeolian or lacustrine sandy sediments. The podzols spread on the Pihkva–Peipsi Lowland are formed on especially poor aeolian sands. Podzols suffer from dryness more than sod-podzols, because they only receive precipitation. Podzols are the poorest soil type in organic matter (OM) and most acid.

METHODS

The humus horizon and parent material of soil have been studied in 82 soil profiles, of them 51% were pseudopodzolic, 20% sod-podzol, 17% brown and 12% podzol soils.

Samples were taken by the vertical furrow method from the walls of excavations penetrating all humus horizons. The cross-section of the furrow varied from 20 to 35 cm^2, seldom more, and the weight of samples was 0.4–0.7 kg. In the course of sampling coarser gravel grains, pebbles and plant roots were removed. The collected material was dried and, using the dry sifting method, the fine fraction <2 mm was separated for analysis with an aluminium sieve. In the laboratory the samples were powdered to the grain size of 0.074 mm using a cast-iron vibro grinder having a low concentration of microelements.

The total contents of all elements were determined by quantitative methods (Table 1): Pb and U by X-ray fluorescence, Cu, Mn and Zn by atomic absorption (extracted in HF, HNO_3 and $HClO_4$ acids), Hg with a gas analyser, and F by an ionselective electrode. All analyses were made of samples dried to constant weight at 105 °C.

Table 1. **The determined elements, the applied methods of laboratory analyses and their detection limits in ppm**

Method of analysis	Cu	F	Hg	Mn	P	Pb	U	Zn
X-ray fluorescence						2	1	
Atomic absorbtion	2			5				2
Gas-analyser			0.002					
Colorimetric					40			
Ionselective electrode		100						

The average contents of elements are presented as geometric means in order to remove the influence of occasional high contents (Григорян и др., 1983), but in Figures 2–6 arithmetical means and arithmetical standard deviations are used.

RESULTS

Analysing the migration of elements it can be concluded that most elements observed (Cu, Mn, P, Pb, Zn) are relatively sedentary in soil profile (Figs. 2 and 3). The content of F and U in the humus horizon is twice lower than in parent material (Figs. 4 and 5), while Hg content in the humus horizon doubly exceeds that in parent material (Fig. 6).

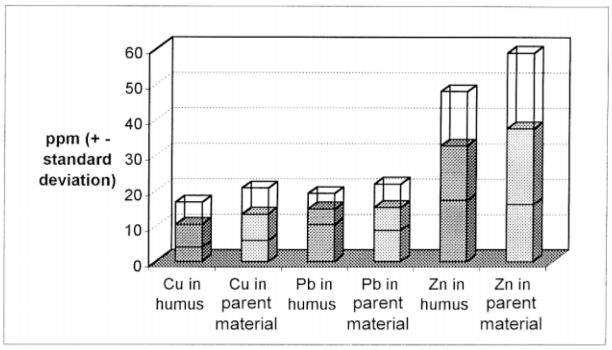

Fig. 2. Content of Cu, Pb and Zn in humus and parent material

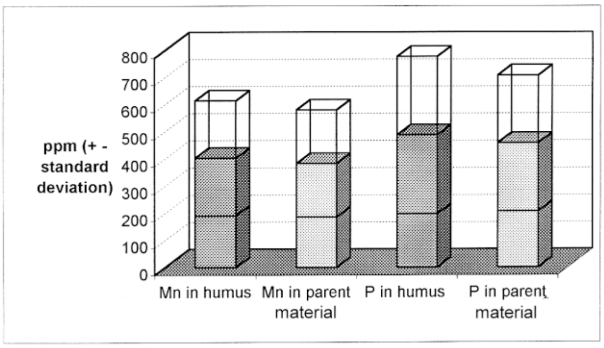

Fig. 3. Content of Mn and P in humus and parent material

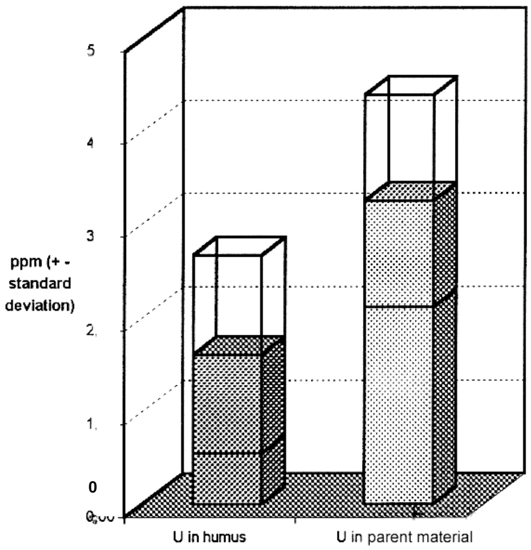

Fig. 5. Content of U in humus and parent material

Among polymetals, Cu is the most mobile element, but at the same time it is easily bound by organic matter (Kabata-Pendias, Pendias, 1992). In the study area, Cu is more mobile than Pb, but similar to Zn (Fig. 2). From brown and pseudopodzolic soils where Cu content in parent material is higher than in podzols and sod-podzolic soils, Cu is carried out from the humus horizon. The process is slower when the content of Cu decreases to 10 ppm or less (Table 2). At this content, OM is probably able to bind a certain content of Cu in the humus horizon.

Sod-podzolic soils contain OM obviously sufficient to bind Cu in the humus horizon, because in these soils the content of Cu in the humus horizon is almost equivalent to that in parent material. In podzols formed from sand the content of Cu is the lowest, but there is too little OM in the humus horizon for binding Cu, and 16% of Cu is leached out from the humus horizon. The content of Cu is relatively variable both in the humus horizon and in parent material, the coefficient of variation fluctuating from 44% in the parent material of pseudopodzolic soils up to 72% in the parent material of

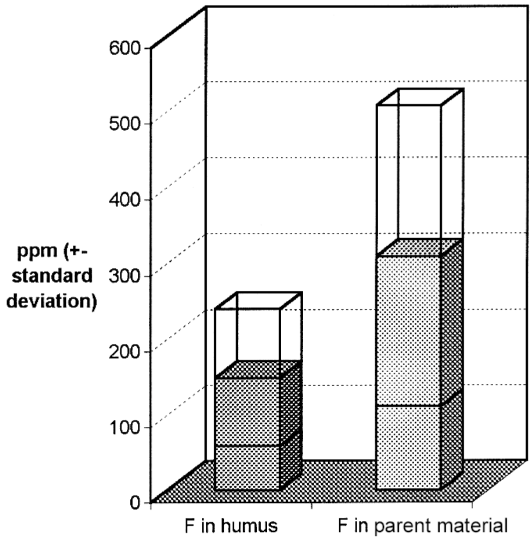

Fig. 4. Content of F in humus and parent material

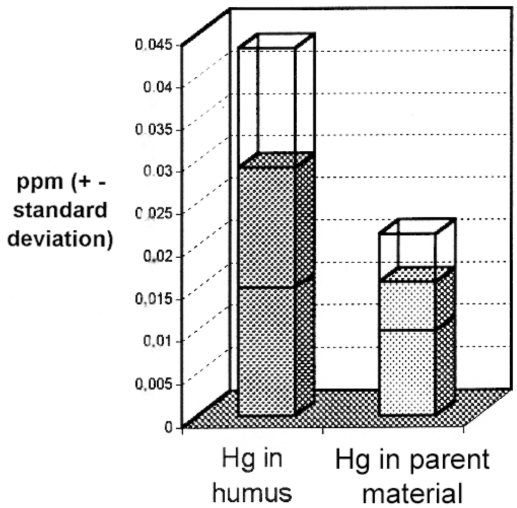

Fig. 6. Content of Hg in humus and parent material

podzols soils and geometric deviation reaching up to 2.1 times (Table 2).

Pb is immobile in all soil types. The coefficient of variation in the humus horizon ranges from 16 to 34% (Table 2). In parent material the variation is also low (25–34%), except podzol soils where the coefficient of variation is 54% and the geometric deviation is 2.3 times. Differently from Cu, Pb content in the humus horizon of brown soil is somewhat (15%) higher than in parent deposits. A similar regularity is observed also in sod-podzolic soils. This process is regarded in both field and forest sampling points, therefore there is no reason to speak about local pollution of soil. However, in all cases Pb is immobile.

Migration of Zn among the soil horizons resembles that of Cu. Zn (Fig. 2), too, is carried out of brown soils, its content is the humus horizon being almost twice lower than in parent deposits. A similar situation is observed in pseudopodzolic soils, but since Zn content in parent material is considerably

Table 2. **Geometric mean, geometric deviation and standard deviation of aritmetical mean of microelement contents in soils**

		Humus of all soils	Par. mat. of all soils	Humus – K0+1	Par. mat. – K0+1	Humus – LP	Par. mat. – LP	Humus – Lk	Par. mat. – Lk	Humus – L	Par. mat. – L
Cu	Geom. mean	9.3	12.3	11.8	16.3	9.6	13.5	9.7	10.1	7.5	8.9
	Geom. st. dev.	1.8	1.8	1.7	2.1	1.5	1.4	1.6	2.0	1.8	2.1
	St. dev.	6.4	7.4	5.9	12.7	7.1	6.2	5.6	6.5	3.7	6.4
	Coeff. of vaiation	**62%**	**59%**	**52%**	**54%**	**63%**	**44%**	**58%**	**65%**	**49%**	**72%**
F	Geom. mean	125	274	238	292	150	292	83	187	50	109
	Geom. st. dev.	2.0	1.8	1.5	2.1	1.5	1.6	1.9	1.5	1	2.5
	St. dev.	91	198	112	295	64	182	67	74	0	138
	Coeff. of vaiation	**61%**	**64%**	**43%**	**80%**	**36%**	**58%**	**67%**	**37%**		**89%**
Hg	Geom. mean	0.029	0.016	0.031	0.014	0.030	0.016	0.021	0.011	0.012	0.017
	Geom. st. dev.	2.0	1.5	1.3	1.3	1.5	1.4	2.4	1.7	2.4	1.6
	St. dev.	0.014	0.006	0.008	0.003	0.014	0.006	0.013	0.008	0.010	0.007
	Coeff. of vaiation	**49%**	**36%**	**25%**	**23%**	**44%**	**30%**	**48%**	**61%**	**80%**	**41%**
Mn	Geom. mean	346	335	470	392	387	392	417	245	143	249
	Geom. st. dev.	1.9	1.8	1.4	1.5	1.6	1.6	1.8	2.0	2.0	2.1
	St. dev.	212	208	150	172	172	205	311	190	104	186
	Coeff. of vaiation	**52%**	**54%**	**31%**	**36%**	**39%**	**45%**	**62%**	**64%**	**55%**	**62%**
P	Geom. mean	419	424	528	519	455	430	319	296	341	404
	Geom. st. dev.	1.9	1.5	1.5	1.2	1.7	1.5	2.1	1.4	1.4	1.8
	St. dev.	312	250	350	123	220	342	214	122	123	242
	Coeff. of vaiation	**63%**	**56%**	**59%**	**23%**	**44%**	**68%**	**53%**	**39%**	**32%**	**50%**
Pb	Geom. mean	13.9	14.2	16.9	13.9	15.0	15.6	12.6	10.8	11.8	13.7
	Geom. st. dev.	1.4	1.6	1.2	1.4	1.4	1.4	1.5	1.4	1.5	2.3
	St. dev.	4.4	6.7	2.7	3.8	4.4	4.5	4.5	3.9	2.5	6.6
	Coeff. of vaiation	**30%**	**43%**	**16%**	**25%**	**27%**	**28%**	**34%**	**34%**	**21%**	**54%**
Zn	Geom. mean	30.4	35.0	39.5	51.8	33.0	39.5	28.7	23.0	14.4	22.6
	Geom. st. dev.	1.7	1.9	1.5	2.0	1.4	1.5	1.5	1.6	2.0	1.9
	St. dev.	15.4	21.4	16.0	38.0	12.7	14.8	9.4	11.8	15.0	17.6
	Coeff. of vaiation	**47%**	**57%**	**41%**	**52%**	**35%**	**33%**	**31%**	**47%**	**72%**	**66%**
U	Geom. mean	1.42	3.05	1.74	3.02	1.50	3.41	1.25	2.87	1.44	1.80
	Geom. st. dev.	1.6	1.5	1.6	1.3	1.7	1.4	1.6	1.6	1.9	2.0
	St. dev.	1.06	1.23	1.20	0.73	1.30	1.16	0.66	1.26	1.21	0.99
	Coeff. of vaiation	**65%**	**35%**	**63%**	**23%**	**71%**	**34%**	**49%**	**40%**	**84%**	**55%**

lower (average 40 ppm), only about 15% is carried out. In sod-podzolic soils where Zn content in the parent material is low (23 ppm), Zn accumulates in the humus horizon, its content being by 15% higher than in parent material. It is very likely that the majority of Zn is bound by OM. In case the OM content in podzol soils is very low, Zn tends to be washed out of the humus horizon. Zn is relatively uniformly distributed, the coefficient of variation in most soil types being below 50%, but it is highly variable in podzol soils where the content of Zn is low both in humus horizon and in parent material. The coefficient of variation is 72% in humus and 66% in parent material (Table 2).

Mn is a plant nutrition element. The average Mn content in the humus horizon and parent material is similar (Fig. 3). Its migration between soil horizons is balanced in brown and pseudopodzolic soils. In sod-podzolic soils Mn concentrates in the humus horizon, the average Mn content in the humus horizon being 1.7 times higher than in parent deposits. Differently from sod-podzolic soils, about one third of Mn is leached out from podzol soils. In the two above-mentioned soil types the variation of Mn content is low, but in sod-podzolic and podzol soils its variability is relatively high in both humus and parent material (Table 2). Usually the variability of element contents is the highest in podzol soils, where their contents are the lowest, but exceptionally Mn is most variable in sod-podzolic soils where the coefficient of variation is 62% in the humus horizon and 64% in parent material.

Migration of P in the soil profile resembles that of Mn. In all soil types the movement of P tends to be similar in the humus horizon and parent material. In brown soil, the content of P in the humus horizon is higher than in parent material, but the content of P is variable. The variation coefficient in humus is 59%, which is especially high as compared to the parent material of this soil type where the coefficient of variation is only 23%. In pseudopodzolic soil, the content of P is equally distributed between the humus horizon and parent material. In sod-podzolic soil, the content of P in the humus horizon is 1.3 times higher than in parent material, but the variation coefficient of the humus horizon is also high (53%) as compared with parent material (39%). An analogous behaviour is exhibited by Mn: its variation is high in soils where the content of this element is higher than in parent material. It should be mentioned that high contents of both P and Mn in humus horizon occur equally in forest and field sampling points, therefore it certainly cannot be due to local pollution.

F and U behave similarly in all soil types, they are carried out from the humus horizon (Figs. 4 and 5). As regards F, the process is most intensive in sod-podzolic soils where F content in the humus horizon is more than twice as low as in parent deposits, but in pseudopodzolic soils the process is of comparable intensity (Table 2). From podzols, too, F is carried out intensively, but in all samples the content of F in humus is below detection limit and therefore it is difficult to draw definite conclusions. The above regularity is observed in almost all samples. The variation of F content is higher in parent material (64%) than in the humus horizon (61%) and varies largely where F content is high (80% in the parent material of brown soils) or the lowest (89% in the parent material of podzol soils).

The migration of U is similar in all soil types, its content in parent deposits being higher than in the humus horizon. The difference is the smallest in podzol soils. However, in this soil type U content is very low and therefore the migration dynamics cannot be clearly followed, since the concentrations are below analysis detection limit. Contrary to F, the contents of U vary more significantly in the humus horizon. The variation of U content is the highest in podzol soils (84%), but it is high in other soil types as well. The variation of U is the lowest in sod-podzolic soil where the average content in the humus horizon is the lowest and the leaching out process is most intensive (Table 2).

Among the elements under observation, migration of Hg is the most interesting (Fig. 6). Hg content in the humus horizon is considerably higher than in parent material, which is due to the OM acting as a sorbent of Hg in this soil type and due to Mg volatility. The regularity is not clearly observed in podzol soils, because there is too little OM to bind essential amounts of Hg. The distribution of Hg in soil is quite uniform as compared with other elements discussed in this paper. The variation of Hg is higher in the humus horizon (49%) than in parent material (36%), except sod-podzolic soils where the situation is reverse.

In podzol soils, the content of Hg varies most (80%) in the humus horizon, but at the same time it is the lowest.

CONCLUSIONS

Considering the above-said, it can be concluded that in Southeast Estonia microelements are selectively carried out from the humus horizon of leached brown and podzol soils.

Cu, Pb and Zn move very little among the soil horizons. Cu and Zn are carried out from humus horizons of most soils studied, except sod-podzolic soils where Zn accumulates and the migration of Cu is balanced.

Mn and P are both nutrient elements; their movement among the soil horizons is balanced. They are carried out from the humus horizon only in podzol soils.

F and U, regarded as pollutants, are both carried out from the humus horizon. This process is observed in all types of soils.

Hg is the only element accumulating in the humus horizon. However, its average content is always low, everywhere being below the maximum permissible concentration.

Brown and all other podzol soils in Southeast Estonia are poor in nutrient elements mainly because of their lack in the parent material of the soils but not because they are carried out from the humus horizon.

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MIKROELEMENTØ MIGRACIJA PIETRYÈIØ ESTIJOS PAGRINDINIØ TIPØ DIRVOÞEMIUOSE

S a n t r a u k a
Nagrinëjama Cu, F, Hg, Mn, P, Pb, Zn, U migracija Pietryèiø Estijos rudþemiø ir jauriniø dirvoþemiø profiliuose. Tyrimø tikslas buvo iðaiðkinti, kodël Pietryèiø Estijoje sumaþëjæ beveik visø elementø kiekiai – ar jie iðneðami ið humusinio horizonto, ar jau ið pradþiø dirvodarinëse uolienose buvo jø maþai.

Tirtø elementø vidutiniai kiekiai yra 1,2–1,7 karto maþesni, palyginti su vidutiniais Estijos elementø kiekiais, tik Hg vidurkis panaðus á jo vidurká visoje Estijoje. Siekiant iðspræsti ðià problemà, minëtø mikroelementø kiekiai tirti rudþemiø ir ávairiø jauriniø dirvoþemiø humusiniame horizonte ir dirvodarinëse uolienose.

Elementø migracijos analizë rodo, kad Cu, Mn, P, Pb, Zn kiekiai dirvoþemio profilyje yra palyginti pastovûs. F ir U kiekiai humusiniame horizonte yra dukart maþesni nei dirvodarinëse uolienose, o Hg kiekis humusiniame horizonte dukart didesnis uþ jo kieká dirvodarinëje uolienoje. Trumpai tariant, pagrindinë prieþastis, kodël Pietryèiø Estijos rudþemiuose ir jauriniuose dirvoþemiuose trûksta mitybos mikroelementø, yra jø menkas kiekis dirvodarinëse uolienose, iðneðimas ið humuso horizonto yra maþiau svarbus.

Raktaþodþiai: dirvoþemio geochemija, mikroelementø migracija, mitybos elementai, pavojingi elementai