The geochemical atlas of the humus soil horizon in Estonia

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The geochemical atlas summarised the result of mapping of humus horizon in Estonia on scale 1 : 500,000.

The atlas contains maps showing the concentrations of B, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sc, Sn, Sr, Th, U, V, Y, Zn, Zr, and organic matter (OM) in humus soil horizon, soil types and their hostrock. The maps (scaled 1 : 1,200,000) were based on the chemical results derived from about 1,550 samples. Together with the explanatory text, the maps give a review of the concentration level of elements in the humus horizon of Estonian soils relative to the land soil concentration pattern. In addition, they include concentrations of elements in basic soil types, and their main distribution regularities, as well as differences in the chemical properties of various soil types.

Furthermore, natural and anthropogenic elemental anomalies, the intensity and distribution of atmospheric pollution are considered.

Final processing of the information collected during geochemical mapping and its preparation for publishing were carried out by a group of Estonian and Swedish authors and was sponsored by Swedish organisation SIDA.

Methodology

The majority of the soil samples used in the atlas were collected from humus horizon of all soil types distributed in Estonia. The density of sampling network was 1 point per 30–35 km^2.

Samples were taken using a furrow method from the excavation wall penetrating all soil horizons. The weight of samples was 0.3–0.6 kg.

The material collected was dried and fine fraction (<2 mm) separated for analyses. Samples from the upper layer of peat were collected from central parts of high bog areas. In lab, the samples of humus horizon were crushed to the grain size of less than 0.074 mm; peat samples were ashed at 450–500°C.

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For determining the concentration of elements in samples, XRF, AAS, flame photometry, gas-analyser, volumetric analysis, coulorimetry, ionselective electrode and semiquantitative spectral analysis methods were used.

The reliability of the laboratory data was checked using the several international and local reference samples and by participating in intercalibration. Control analyses were made at the Swedish laboratory Analytica AB.

The geochemical map is displayed on 31 main and 2 auxiliary sheets. Each main sheet characterises the concentration of one element or OM content and its distribution in the section of main soil types. On the geochemical map sheets the size of the circle indicates the element's concentration at a certain point, and it colour marks the most probable soil type at the sampling point. All the maps shows the average element concentration of the humus horizon of Estonia soils (from x:1.14 to x . 1.14) is denoted by a circle 2 mm in diameter. The average of land soil is shown by yellow colour.

Main results

In the humus horizon of Estonian soils, the increased or high concentrations of microelements (Cd, F, Mo, P, Pb, U, Zn) are quite common. They results mostly from the occurrence and heterogeneous distribution of *Dictyonema* shale, phosphorite, and crushed varieties of bedrock subjected to polymetallic mineralization, in the parent deposits of soil. High concentrations of microelements are partly related to the rocks dereved from the Fennoscandian Shield.

The elements are provisionally divided into three groups, according to their average concentrations in the humus soil horizon. The first group includes B, Ca, Cu, K, Mg, Mn, Mo, Na, P and Zn. These elements concentrate in plants. Undoubtedly, these elements serve as nutrients for plants. The humus horizon of Estonian soils is poor in nutrient elements.

The elements of the second group do not concentrate in plants. Such elements are Ba, Be, Cd, F, Fe, Hg, Nb, Sn, Sr, U and V. Their average concentrations in the humus horizon are low. Only the concentrations of uranium, and in many regions also fluorine generally exceed the soil clark.

The third group comprises the elements having similar concentration in plant ash and soil. Of the elements considered in the atlas, Co, Cr, Ni, P and Rb, most probably also Sc, Th and other biologically less studied elements, belong to this group. The concentrations of this elemental group in the humus horizon is lower or approaches the soil clark, except the average concentrations of lead, which is about 1.6 times higher than the clark.

The average contents of elements and their distribution pattern in the humus soil horizon has different reasons. Based on the information presented above, the following causes can be indicated:

1. A great share of poorly mixed carbonate rocks, sandstones and siltstones characterised by different macroelement and low microelement concentrations in the parent soil deposits. The presence of bedrock clays, *Dictyonema* shale, phosphorite and the material from the Fennoscandian Shield in the parent soils, generally contribute to such heterogeneity;

2. Neutralisation of soil acidity. Large amounts of oil shale fly ash rich in Ca, Fe, K, Mg, Mo, P, U and other elements were added to the humus soil horizon during the period of socialist agriculture;

3. The ratios of elements carried out by streams as a result of weathering and denudation of the humus horizon, and elements derived from the atmospheric fallout.

In general, atmospheric pollution is the most important contaminant of the humus soil horizon. It is reflected in the upper layer of high bog peat.

At present, in Estonia two major sources of anthropogenic pollution of soil are known: the surroundings of Sillamäe waste depository and the places of fires that have occurred recently in some areas of military objects of the former Soviet Army. In these areas the concentrations of heavy metals sometimes exceed the PCL for tens of times.

The intensive outwash of Ca and Mg, as well as Na takes place in the entire area of Estonia. Considering the data presented in the atlas, we can estimate the approximate amounts of elements per 1 m^2 of land area, carried into the Baltic Sea by surface waters: Ca — 10–15 g, Mg — 2–3 g, Na — 0.4–0.6 g. These values exceed the atmospheric influx for several times. The same relation applies also to potassium.

As for the heavy metals (Cd, Cu, P, Zn), the situation is different. The atmospheric influx of these elements exceeds the their outflow via streams for about two to four times. As the investigations conducted during several decades have revealed no increase in the mineral and heavy metal concentration in groundwater, it can be concluded that the humus soil horizon of Estonia has become enriched with heavy metals, Si, Al and Fe, and depleted in Ca, Mg, Na, and in K.