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Mineral composition and its relations to readily available element concentrations in cultivated soils of Finland

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ABSTRACT

Mineral composition is a fundamental feature that affects the properties and functions of soil through physical, chemical and biological interactions. However, comprehensive knowledge on the mineralogy of agricultural topsoils of Finland has been lacking. In this study, the mineral composition of 120 soil samples included in the national monitoring of agricultural soils of Finland was determined using state-of-the-art quantitative x-ray diffraction analysis by a prior measured full pattern fitting methodology. Quartz, plagioclase and K-feldspar were found to be the dominant soil mineral components. Amphiboles and micas were also common, and several other mineral phases were detected in small quantities. The relative proportions of quartz and plagioclases increased and those of mica, goethite, disordered clay minerals, kaolin and amorphous inorganic components decreased as the soil particle size increased. Compositional statistical analysis discerned a positive association between the prevalence of 12 elements and organic matter and surface-active minerals (goethite, chlorite, disordered clays, kaolin and inorganic amorphous materials), whereas micas contributed to the prevalence of K. The present data agreed with general conceptions of Finnish soil mineralogy but revealed novel details in the mineral composition. The relationship observed between soil textural and mineral compositions supports the current texture-based soil classification system and recommendations.

ARTICLE HISTORY

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KEYWORDS

X-ray diffraction (XRD); quantitative mineralogy; soil monitoring; soil texture

Introduction

As the structural components of soil inorganic matrix, minerals have a strong influence on the properties of soils. Through impacts on aggregation, shrinkage behaviour and plasticity, mineral composition affects soil stability (Locat et al. 1984; Six et al. 2000; Gray and Allbrook 2002; Denef and Six 2005). Consequently, characteristics like erodibility, susceptibility to seal formation and rates of water infiltration and runoff are dependent on soil mineralogy (Stern et al. 1991; Lado and Ben-Hur 2004). Soil mineral surfaces also contribute to stabilisation of organic matter via organo-mineral associations, which influence the spatial distribution of soil microbiota (Kögel-Knabner et al. 2008). In addition, soil mineralogy and biology interact through nutrient cycling because nutrients are mobilised from minerals by biogeochemical weathering (Landeweert et al. 2001). Mineral composition accounts for the inherent fertility of soils (Jackson and Sherman 1953) but the mobility and availability of nutrients is likewise highly dependent on soil minerals (Sollins et al. 1988).

Despite the strong relationship between the mineral composition and properties of soil, the mineralogy of cultivated soils of Finland has attracted little attention. Extensive surveys have focused on mineral exploration of basal tills (Koljonen 1992; Mäkinen 1992; Lintinen 1995; Peuraniemi et al. 1997). In the 1970s, Sippola (1974) determined the mineral composition of 56 agricultural subsoil samples collected mostly from southern Finland. He used both differential thermal analysis and X-ray diffraction (XRD) analysis for identification of the minerals. The identified phases were then determined semi-quantitatively by a combination of thermal weight loss, cation exchange capacity, specific dissolution and total elemental composition data. More recently, semi-quantitative mineral data acquired by XRD has been reported for various single cultivated

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soils in relation to characterisation of soil pedons (e.g. Åström and Björklund 1997; Mokma et al. 2004; Yli-Halla et al. 2006; Yli-Halla et al. 2009).

The soils of Finland formed during and after the Weichselian glaciation when the ice sheets crushed and ground the underlying bedrock and the melting waters further transported and sorted the debris (Koljonen 1992). The time of weathering has been short (ca. 12 000 years), and the mineralogy of the soils thus reflects that of the bedrock, which consists mainly of granites, migmatites and schists (Koljonen 1992). However, the fine silt and clay fractions typically represent material from a wider area than coarser particles of more local origin (Taipale et al. 1986). Agriculture mostly occupies clays, silts, fine-rich tills and organic deposits (mull and peat) in the southern and western regions of the country, but crop production extends to the eastern border with Russia and north up to the Arctic Circle (Heikkinen et al. 2013).

The objective of this study was to deepen the basic knowledge of the mineralogy of arable topsoils of Finland by providing, for the first time, quantitative mineral data determined by state-of-the-art full pattern fitting of prior measured XRD patterns of samples with extensive geographical coverage. The dependence of mineral composition on soil type was assessed in four soil type classes based on texture and organic matter content. In addition, the relations of various readily available element concentrations to soil composition were explored to elucidate the link between soil mineralogical composition and fertility.

Material and methods

Studied soils

Soil samples from the national monitoring of agricultural soils of Finland from 2009 were used in the study. The monitoring network, which covers the whole agricultural area of the country, was initially launched in 1974 (Sippola and Tares 1978) and re-sampled in 1987 (Erviö et al. 1990), 1998 (Mäkelä-Kurtto and Sippola 2002), 2009 (Heikkinen et al. 2013; Keskinen et al. 2016) and 2018 (Heikkinen et al. 2021, 2022). The 2009 campaign comprised 611 samples collected from GPS-located sites (Figure 1) by bulking about 10 subsamples taken with a soil auger (\emptyset 2 cm) from the 0 to 15 cm surface layer of a 10 m × 10 m sampling area. Thereafter, the soils were air dried, ground to pass through a 2-mm sieve and stored in cardboard boxes at room temperature until subsampled for the current study in 2014.

In the monitoring study, the samples were analyzed for electrical conductivity (EC), pH (H_2O) and 0.5 M



Figure 1. The sampling sites of the national monitoring of agricultural soils of Finland from 2009. Sites included in the current study are marked with dark circles. Regional division into North, South, East and West delineated with grey lines is referred to in Table 1.

ammonium acetate-acetic acid (AAAc, pH 4.65) extractable Ca, K, Mg, P and S (Vuorinen and Mäkitie 1955; Keskinen et al. 2016). Concentrations of Cu, Fe, Mn, Al, Zn, Cd, Co, Cr, Mo, Ni and Pb were determined from AAAcacid ethylenediaminetetraacetic (EDTA) extracts (Lakanen and Erviö 1971), and that of B from hot water extracts (Berger and Truog 1944). In addition, organic C content was analyzed by dry combustion (Heikkinen et al. 2013) and converted to organic matter content using the van Bemmelen factor (1.724) later confirmed suitable for the Finnish arable soils by Heikkinen et al. (2021). Particle size distribution was determined by the pipette method of Elonen (1971). The above-described chemical analyses were carried out at the laboratories of the Natural Resources Institute Finland in Jokioinen (data is given in supplementary information, Appendix 1) and the textural analysis at Eurofins Viljavuuspalvelu Oy, Mikkeli, Finland (Appendix 2).

In the earlier studies of temporal trends in the monitored variables, the data were grouped by region and soil type (Heikkinen et al. 2013; Keskinen et al. 2016). In the present study, the regional examination was omitted due to the limited number of samples, but the same soil type classification, which was based on the organic matter content and texture of the samples, was adopted. The only exception was that mull (20-40% organic matter) and peat (more than 40% organic matter) soils were combined to a single class of organic soils. Mineral soils (containing less than 20% organic matter) were classified into clay, fine and coarse soils according to the geotechnical soil classification system (Korhonen et al. 1974). Clays contain more than 30% of size fraction less than 0.002 mm, fine soils are dominated by particles finer than 0.06 mm but contain less than 30% clay-sized particles, and coarse soils comprise mostly particles coarser than 0.06 mm.

Sample selection

Mid-infrared (MIR) spectroscopy was used to select a subset of samples representing maximal variability in the data. The MIR spectrum serves as a generic indicator of the soil characteristics since it responds to both the mineral and organic composition of the soil (Shepherd and Walsh 2007). An MIR spectrum was recorded for all the 611 samples (Bruker Tensor 27 HTS-XT) at the Soil-Plant Spectral Diagnostics Laboratory of the World Agroforestry (ICRAF) in Nairobi, Kenya. Thereafter, a PCA analysis was performed on the spectral data and the Kennard-Stone algorithm (Kennard and Stone 1969) applied for sample selection. Out of the 611 monitoring sites, samples of 120 sites were selected for the XRD mineral analyses. The numbers of selected samples on each of the five soil classes are given by region in Table 1 and the location of the sample sites included in the study in Figure 1.

XRD analyses

For XRD, the 120 selected samples were pre-ground (<1 mm) and air-dried (40°C) then micronisied with a McCrone Mill (3 g for 12 min) using ethanol as the grinding fluid, centrifuged, re-suspended with hexane, oven-

Table 1. Distribution of samples selected to XRD mineral analyses by region and soil class. For the geography of the regions, please see Figure 1.

Soil class	South	East	West	North	Total	
Clay	18	2	1	0	21	
Fine	12	9	11	5	37	
Coarse	7	10	16	6	39	
Mull	3	4	0	1	8	
Peat	1	6	2	6	15	
Total	41	31	30	18	120	

dried and passed through a 250 µm sieve. The resulting powders were top-loaded into circular 25 mm diameter holders and a flat specimen surface obtained by a chopping action with the sharp edge of a razor blade, taking care, as far as possible, to try to avoid inducing preferred orientation. XRD patterns of the specimens were recorded at ICRAF using a Bruker D2 Phaser diffractometer with Ni-filtered, Cu radiation with the X-rav tube operated at 30 kV and 10 mA. The beam was collimated using a 0.6 mm divergence slit, a 1 mm antiscatter slit and a 2.5 mm Soller slit. Samples were rotated continuously at 15 rpm during data collection over the angular range of 3-75 °20, counting for 96 s per 0.02° step with a Lynxeye position sensitive detector. The minerals present in the samples were identified using the Powder Diffraction File database (Gates-Rector and Blanton 2019) and data in the monograph of Brindley and Brown (1984).

Quantification of the soil components

Quantitative analysis of the XRD data were made using a prior determined full pattern fitting approach as described by participant #18 in Omotoso et al. (2006) and as more recently implemented in the 'powdR' package (Butler and Hillier 2020; Butler and Hillier 2021) of the R language and environment for statistical computing (R Core Team 2020). Measured patterns were fitted using a set of 86 reference patterns covering the range of minerals identified. The reference pattern library used was a hybrid library composed of patterns from the RockJock library of Eberl (2003) plus additional standard patterns for quartz, various feldspars, iron oxides, amphiboles and clay minerals that had been run as standards on the Bruker D2 at ICRAF to facilitate quantification of soil XRD patterns recorded on this instrument; both libraries are now included in the 'powdR' package (Butler and Hillier 2020). In total 86 standard patterns were selected for use in the full pattern fitting process, 15 of which were measured on the D2 at ICRAF. The large number of standard patterns arises due to the inclusion of several patterns for the same mineral or mineral group, e.g. the plagioclase feldspars were represented by nine standard patterns. Patterns to account for scattering from soil organic matter were also included as well as patterns for soil paracrystalline phases such as ferrihydrite and allophane. All soil samples were quantified in exactly the same way using the fps function in powdR. An example of a fitted pattern for a clay soil is given in Figure 2 and for the other soil types in supplementary material (Appendix 3). The example shown in Figure 2 is not exceptional and all fits were of a similar high guality, as can be



Figure 2. Full pattern fit for a clay soil in Southern Finland. Black line indicates the measured XRD pattern and red the calculated XRD pattern (note the square root intensity scale).

judged objectively by the Rwp value, which was used as the objective function in powdR (Butler and Hillier 2020, 2021) and ranged between 0.0339 and 0.1185 (see supplementary material Appendix 2), and as assessed visually by comparison of measured and calculated patterns. Of the 86 patterns selected to make the fits to the soils, 72 were retained by the fps function and the final mineralogy was summarised into 25 different minerals or mineral groupings. For the data analysis, a further reduction to 12 minerals or mineral groupings was performed. To assess the compositions in the mineral fraction, the data were normalised to exclude the share of the organic fraction. The complete tabulated data set, along with additional details of mineral groupings used in the data analysis, is given in supplementary information (Appendix 2). It is pertinent, however, to indicate that the grouping referred to as 'disordered clays' is an aggregation of all types of expandable (swelling) 2:1 layer clay minerals, i.e. it includes smectites, vermiculites and mixed-layer clays with obvious expandable components. Additionally, it is important to note that the full pattern fitting method does not use or require an added internal standard for the quantification of amorphous phases. This is because such phases are quantified directly in the full pattern fitting approach by inclusion of reference XRD patterns, even though such patterns may show no evidence of Bragg diffraction.

Data analyses

The mineral composition data exhibits a statistically special structure because its components carry only relative information as they constitute weights that sum up to a constant. Therefore, standard statistical methods are not applicable, but rather specialised methods intended for compositions are needed (for a detailed reasoning, see Aitchison (1986) and Appendix 4).

In this study, two model scenarios were considered. In model 1 (M1): the mineral composition of soil mineral phase, i.e. the organic fraction excluded, (compositional response) was assessed with the different soil types (4 categorical levels).

In model 2 (M2): the relations between readily available elements (one-dimensional response) were modelled against the soil composition including the mineral (n = 12) and organic (n = 1) fractions (composition).

For both M1 and M2, their detailed descriptions are given in Appendix 4. For M1, the model intercept is interpreted as the expected composition at the baseline level of the predictor. For a categorical predictor, compositional results are commonly presented as the estimated composition for each level of the categorical predictor. We used MANOVA to test the statistical significance of the predictor overall as well as the differences between predictor classes. Variation of the compositions was calculated using bootstrapping.

For M2, type 3 MANOVA tests were performed to test the statistical significance of the mineral compound as a predictor. Furthermore, the coefficient of determination R^2 was calculated to assess the predictability of each model. From the modelling results, we can infer the components which have the greatest influence on the response.

The mineral composition data encompassed 147 zero-values, which are not allowed in the compositional analysis. Therefore, a small nonzero value (1^{-1000}) was imputed to replace each zero, after which the closure operation was performed. Thus, the final dataset contained no strict zero values. The selected nonzero value was the highest number after which its reduction had no effect on the outcome of the model.

The statistical analyses were performed using the R software (R core team 2020) and its packages *compositions* (van den Boogart et al. 2021), *tidyverse* (Wickham et al. 2019) and *xlsx* (Dragulescu and Arendt 2020).

Results and discussion

Quartz, plagioclase and K-feldspar were discerned as the main mineral components of agricultural topsoils of Finland (Table 2, Appendix 2). Some amphiboles were found in all the studied samples and nearly all samples also contained micas (dioctahedral, trioctahedral or both). Epidote, goethite, chlorite, kaolin, disordered clays (including vermiculite and smectite) and amorphous inorganic components (e.g. ferrihydrite) were commonly present in small quantities. Pyroxenes, garnets, hematite, magnetite, ilmenite, rutile, anatase,

Table 2. Compositional means (%) for the mineral contents including organic matter in the entire data set of 120 agricultural soils.

Mineral	Compositional mean (%)
Quartz	32.6
Plagioclase	25.9
K-feldspar	10.9
Amphibole	5.0
Epidote	0.6
Goethite	0.5
Mica	5.4
Chlorite	0.9
Disordered clays	1.8
Kaolin	0.1
Amorphous inorganic	1.4
Trace phases	0.9
Organic	14.0

calcite, dolomite and talc occurred less prevalent in minor amounts and in the presentation of the results are combined to form a group of 'trace phases'. In these inherently acidic soils, calcite and dolomite can be assumed to represent residues from liming (see Keskinen et al. 2016). Overall, the major mineralogy was granitic in type and agreed with the main findings of the previous survey on agricultural soils by Sippola (1974). As Lintinen (1995) has stated, the mineralogy of the Finnish bedrock is rather monotonous leading to fines largely similar in mineralogy.

A comparison between the mass proportions of soil textural clay and mineralogical clay in the soil mineral phase is shown in Figure 3. Textural clay is defined as the particle size fraction of <0.002 mm, whereas for mineralogical clay two alternative specifications were considered: (1) the sum of chlorite, disordered clays, and kaolin, and (2) the sum of all clay/phyllosilicate minerals, which is the former plus the micaceous minerals. As seen in the figure, only at low clay contents (< 30% textural clay of the soil inorganic phase) does the proportion of mineralogical clay sometimes exceed that of the textural clay, particularly if the micas are included in the definition of mineralogical clay. In clay soils (>30% textural clay), the proportion of clay minerals, irrespective of definition, was consistently lower than the corresponding textural fraction. Similarly, Sippola (1974) reported the coarse clay size fraction (0.2–2 μ m) of Finnish cultivated subsoils to contain roughly 30% micas and up to 50% K-feldspar, plagioclase and guartz. Feldspars, guartz and amphiboles were also



Figure 3. The relationship between proportions of textural clay (<0.002 mm size fraction) and mineralogical clay in the soil mineral phase. Mineralogical clay is defined either as the sum of chlorite, disordered clays and kaolin (full circles) or as all clay/phyllosilicate minerals (open circles). The solid line denotes equal values. n = 97 (organic soils are omitted due to missing textural data)

commonly found in the clay fraction of basal tills (Lintinen 1995; Peuraniemi et al. 1997). The felsic minerals have also been found to dominate the mineralogical composition of the clay size fraction in eastern Canadian postglacial clays (Locat et al. 1984). These patterns imply that glacial action has ground hard rock-forming minerals to small size fractions such that they are common in the clay size fraction.

The amount of organic matter in the current set of soils ranged from 2.3% in a coarse mineral soil to 85% in a peat soil (Figure 4). Comparison of the organic matter content determined from the XRD pattern and based on direct C analysis yielded comparable results. Although XRD is commonly used mainly for identification and quantification of crystalline compounds, it is apparent that the full pattern fitting method of quantification can be used to make a reasonable estimate of soil organic matter content, although one that is unlikely to be as accurate as that based on C content, particularly at low levels.

Mineral composition in different soil types (M1)

Each soil type (clay, fine, coarse, organic) embodied a mineral composition differing from the others (*p*-value < 0.01) (Figure 5). Quartz and plagioclases were the main components of the mineral matter in all soil types, but their relative proportions increased as the grain size increased. Mica, goethite, disordered clays, kaolin and amorphous inorganic components, in contrast, were most abundant in clay soils and their proportion diminished with increasing grain size. In organic soils, the share of amorphous inorganic matter was exceptionally high. It is not known currently if this is a real feature or an issue associated with the full



Figure 4. Relationship between soil organic matter contents determined via dry combustion and XRD. The solid line denotes linear regression ($R^2 = 0.96$, n = 120).

pattern fitting process, such that the fit to the high organic matter is improved by the addition of the patterns of the inorganic amorphous phases.

The results broadly agree with previous more local semi-quantitative data (Åström and Biörklund 1997; Mokma et al. 2004). However, the new detailed guantification of the mineral composition gives novel information on the mineralogy of Finnish agricultural soils as mineral phases that were not identified by the traditional semi-quantitative method were now observed. For example, in the previous relatively extensive work of Sippola (1974), amphiboles, epidote, goethite, kaolin and trace phases were not specified. However, the current relative proportions of quartz, plagioclases (Naand Ca feldspars), K-feldspar and amorphous materials were in the range reported by Sippola (1974). In his work, the proportion of chlorite was clearly higher in comparison to the present study and in fine-textured soils, the share of mica tended to exceed the current values. In contrast, the proportions of disordered clays were clearly higher in the fine and coarse soils of the present study than in the corresponding soil types in Sippola's (1974) material. The general trends of increase in guartz and plagioclases and decrease in amorphous inorganics (allophane, ferrihydrite), disordered clays and mica with increase in particle sizes were consistent in both the surveys. In contrast to the international soil classification system based on a wide variety of soil features (IUSS Working Group WRB 2015), in Finland soils are typically classified simply by texture. The observed mineralogical uniformity within the textural classes supports this straightforward approach in practical agricultural context.

Relation of mineral composition to soil chemical properties

Several discernible relationships were identified between the mineral composition and the prevalence of readily available elements in soil (Table 3). Mineral and organic soil surfaces control the retention and transport of elements and compounds in soil through their active polar sites (isomorphic substitution sites, mineral edges and ionised functional groups) and nonpolar sites (neutral mineral surfaces and hydrophobic parts of organic matter) (Johnston and Tombácz 2002). The observed positive effect of goethite on the prevalence of Ca, Mg, B, Co and Pb may reflect the high universal adsorption capacity of this common weatheringinduced oxyhydroxide (Liu et al. 2014). Chlorite, disordered clays, kaolin and inorganic amorphous materials, which were also linked with the abundance of various elements in the compositional analysis, are likewise



Figure 5. Mean estimates of the mineral compositions in the mineral fraction of different types of cultivated topsoils in Finland. The error bars denote bootstrapped quantile values of 2.5% and 97.5%.

active soil components possessing high surface areas, structural charges and reactive surface functional groups within the limits of their structure and composition (e.g. Sposito et al. 1999; Al-Ani and Sarapää 2008; Gypser et al. 2018). As for micas, both in the current and Sippola's (1974) work their contribution to the prevalence of K was significant. Mica minerals (e.g. biotite, phlogopite, muscovite, illite) are known as sources (and sinks i.e. fixation) of K as it occurs as an interlayer cation between the fundamental 2:1 silicate layers (Pal et al. 2001; Barré et al. 2007; Vetterlein et al. 2013; Sarikhani et al. 2018). Though in the compositional data analysis, a weak positive association was found also between micas and the abundance of P, Cu and Pb, no similar direct relationship as with K can be attributed to these elements. Organic matter was linked to the prevalence of many elements, which reflects its key role in soil as an element reservoir (Manlay et al. 2007), binder of metals (Simpson et al. 2002; Wagai et al. 2013), and major contributor to the cation exchange capacity (Parfitt et al. 1995; Krogh et al. 2000). The positive effects of plagioclase on the occurrence of several minor elements and epidote on Zn and Pb are difficult to interpret and may be caused by unidentified interlinkages to other soil properties.

Overall, the explanatory power of soil mineral composition on the prevalence of readily available elements was rather weak (Table 3). However, the soil available element contents could be expected to reflect the elements contained in the soil-forming minerals more directly in native soils than in the cultivated soils that regularly receive external inputs in the form of fertilisers, liming materials, soil conditioners and pesticides. In a recent study, Butler et al. (2020) showed the soil mineral composition to control both total and phytoavailable nutrients in the soils of sub-Saharan Africa, where fertiliser use is still very limited. Their study focused on subsoils to avoid anthropogenic influences. In the anthropogenically affected soils studied here, the presence of various elements may be governed by

Table 3. Relation of mineralogy on the prevalence of easily	available elements in cultivated top	osoils of Finland
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	Al	В	Ca	Cd	Co	Cr	Cu	Fe	К	Mg	Mn	Мо	Ni	Р	Pb	S	Zn
p	***	***	***	***	***	**	***	***	**	***	*	***	***	***	***	***	***
R ²	0.47	0.59	0.43	0.54	0.36	0.17	0.36	0.56	0.14	0.43	0.11	0.24	0.41	0.22	0.65	0.28	0.52
Quartz																	
Plagioclase					+	+	+	+			+		+			+	+
K-feldspar																	
Mica							+		+					+	+		
Amphibole																	
Disor. clay					+	+											
Inorg. am.							+										
Chlorite														+			
Trace phases														+			
Epidote															+		+
Goethite		+	+		+					+					+		
Kaolin														+			
Organic	+	+					+						+		+	+	+

Notes: Significant models are marked with a star sign (***p < .001, **p < .01, * p < .05). Positive associations according to compositional modelling^a (modeling scenario M2) are marked with a plus sign (+). R^2 = coefficient of determination. ^aSee Section 2.5 and Appendix 4.

farming practices and the general element retention capacity of the soil. In the study of Sippola (1974), the clay size fraction was found to be more important than any single mineral constituent in explaining variation in the easily available elements in cultivated soils though the abundances of exchangeable Ca and Mg were also associated with vermiculite. In the African soils, 2:1 phyllosilicates proved to be the main source of extractable nutrients (Butler et al. 2020).

Conclusions

This study revealed that:

- Quartz, plagioclase and K-feldspar were the main components of the mineral phase in agricultural topsoils of Finland.
- Amphiboles, micas (dioctahedral, trioctahedral or both), epidote, goethite, chlorite, kaolin, disordered clays (including vermiculite and smectites) and amorphous inorganic components (e.g. allophane and ferrihydrite) were commonly present in smaller quantities.
- The relative proportions of quartz and plagioclases increased as the soil grain size increased, whereas mica, goethite, disordered clays, kaolin and amorphous inorganic components were most abundant in clay soils and diminished with increasing grain size.
- The textural clay fraction (<0.002 mm) was not only composed of clay minerals but included on average ca. 60% finely ground rock-forming minerals. In organic soils, the share of amorphous inorganic matter was relatively high.
- Relations of mineral composition to easily available element concentrations in soil were detected though the explanatory power of the mineralogy was not strong in general.

 Organic matter and surface-active minerals (goethite, chlorite, disordered clays, kaolin and inorganic amorphous materials) showed a positive effect on the prevalence of several elements indicating their importance as element reservoirs, whereas micas were found to contribute on available K concentrations.

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Disclosure statement

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