

Investigation of the Effect of Soil Mineral Composition on Soil Organic Matter Stability

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Abstract

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The soil organic matter (SOM) pools with different stability play different roles in the agricultural and environmental processes, e.g. in the global carbon cycle. In this work Rock-Eval (RE) pyrolysis measurements and mathematical deconvolution of RE pyrograms were used for determining the abundance, quality, and main biological sources of SOM, as well as for evaluating the relative proportion of the labile (fresh plant and litter) and resistant (lignin and cellulose) bio-macromolecules, immature (humic substances) and mature refractory (naturally stable biological compounds, organic matter stabilized by physico-chemical processes and black carbon) geo-macromolecules. The samples were taken from the A-horizons of Leptosol, Luvisol, and Acrisol formed under different soil conditions (mineral composition, pH, and leaching). In agreement with the present vegetation, bulk RE data together with the results from the mathematical deconvolution of pyrograms display terrigenous plant remnants as precursors of SOM for all the three samples. The presence of the more stable components, indicated by our results in the A-horizon only of Luvisol and Acrisol, could be a consequence of the intense leaching. In contrast, due to the limited leaching, the soluble components also remained in the A-horizon of Leptosol, for this reason SOM seems to be relatively well preserved. The comparison of the results measured and calculated on whole soil samples and their mineral-free hydrolysis-resistant macromolecular fractions (ROM) reveals that the stabilization of SOM is mainly controlled by organo-mineral association in Leptosol and Luvisol. These results suggest the importance of iron-oxides and -hydroxides and clay minerals in the stabilization of SOM for Leptosol and Luvisol, respectively, whereas in Acrisol the stability of SOM is due to the high relative contribution of naturally stable organic compounds.

Keywords: organo-mineral association; Rock-Eval pyrolysis; thermal stability

The soil organic matter (SOM), which is the largest source and sink of terrestrial carbon dioxide (GLEIXNER *et al.* 2001; HEIMANN & REICHSTEIN 2008), plays a significant role in the carbon cycle, several environmental processes (e.g. pedogenesis and migration of pollution) (WATTEL-KOEKKOEK *et al.* 2001; DISNAR *et al.* 2003) and is one of the most important factors for soil fertility. It ensures the acid/base effect of soil, generating proper soil structure and giving appropriate nutrient, heat and water management (STEFANOVITS *et al.* 1999; BRUUN *et al.* 2010). However, SOM is very heterogeneous. It consists of organic compounds with different stability and degradation stage, which are continuum between

biological tissues and humic substances and can be mixed with various anthropogenic substances (SEBAG *et al.* 2006). Nowadays researches are increasingly focused on investigating the stability and preservation of SOM in order to better understand SOM dynamics and role in soil processes (e.g. LÜTZOW *et al.* 2006; MIKUTTA *et al.* 2006; BRUUN *et al.* 2010). In this study, Rock-Eval (RE) pyrolysis – a technique originally designed for petroleum exploration – was used for the characterization of the SOM stability. However, recently RE application has been expanded for the examination of SOM in soils and recent sediments. This technique is applied for temperature programmed heating of a small amount of sample in

an inert atmosphere. The measurement takes only a few minutes so it provides a rapid and cost-effective analysis. RE pyrolysis is a reliable method for determining the amount, quality, and degradation stage of SOM by basic data of RE (e.g. total organic carbon contents (TOC), thermal maturity (T_{max}), hydrogen index (HI), and oxygen index (OI)). In addition to these bulk RE data, the relative contribution of labile (fresh plant and litter) and resistant (lignin and cellulose) bio-macromolecules, immature (humic substances) and mature geo-macromolecules (naturally stable biological compounds, OM stabilized by physicochemical processes and black carbon) can be estimated by the mathematical deconvolution of RE pyrograms (SEBAG *et al.* 2006). Furthermore, the composition of source material and the degree of preservation of the primary biomass can also be estimated by the contribution of the fractions with different thermal stability. Although the biological source material of SOM and its degradation stage are the key factors, environmental and soil conditions also influence the SOM stability. The stability of SOM depends mainly on the chemical composition of organic matter (ZEGOUAGH *et al.* 2004), as well as on the mineralogy (TOMBÁ CZ *et al.* 2004; MIKUTTA *et al.* 2006) and pH (TOMBÁ CZ *et al.* 2004; TONON *et al.* 2010) of the soil. The sorption of SOM to mineral surface is the most important process in the stabilization of SOM, mainly in forest soils. The role of the individual mechanisms is controlled by many factors and different factors can increase or decrease the effect of each other.

This study investigated the stability of three soil samples, the OM of which was formed from similar vegetation under different soil conditions (pH, mineral composition, and leaching). Samples were taken from A-horizons of the three soils: Leptosol, Luvisol, and Acrisol. SOM stability was determined both on the whole soil samples and on the most resistant soluble- and mineral-free organic matter fraction (ROM) using bulk RE data and ratios calculated from mathematical deconvolution of RE pyrograms. We tried to find the main factors resulting in different SOM stability in the studied soil samples.

MATERIAL AND METHODS

All of the investigated soils were formed in temperate climate conditions under continental influence. The average annual rainfall ranges between 600–800 mm.

The studied Leptosol is taken from Aggtelek Karst (48°28'23"N, 20°32'36"E), the vegetation is dominated by deciduous forests (beech and oak). Its parent material is composed of a mixture of weathered Mesozoic limestone and residuum of a relict soil formed of red clay. The C-horizon of this lithomorphous soil is covered directly by A-horizon and illuvial (B) horizon was not developed. According to the World Reference Base for Soil Resources (WRB), the studied sample is classified as haplic Leptosol (calcaric, humic) (FAO 2006).

The studied Luvisol is taken from the Karst plateau of Bükk Mountain (48°7'32"N, 20°39'7"E), the dominant vegetation consists of hornbeam and oak. The parent material of this soil is calcareous sandy sediment deposited on the limestone during the last marine flooding 15 million years ago. Clay minerals, iron, and aluminum oxides and hydroxides, formed by moderate stage of weathering, were leached from the topsoil to accumulate in the subsoil. According to the WRB, this soil is classified as Cutanic Luvisol (ruptic, endoclayic).

The studied Acrisol was taken from the Sopron Mountains (47°39'39"N, 17°33'68"E) which are the eastward extension of the Eastern Alps. In contrast with the previous soil samples, climate is subalpine with not too hot summer and relatively mild winter. The vegetation is dominated by deciduous mixed forests of beech and oak dotted with pines. The litter which covers the topsoil is significantly thicker than in other soil samples and the composition of the litter slightly differs from that of the soils mentioned above. The parent material of the studied soil profile is whiteschist with high magnesium content. It is a strongly acid, podzolic soil where the decomposition of organic matter (OM) and clay minerals has been started. Intense leaching of soluble OM and mobile compounds from the weathered minerals resulted in the accumulation of OM, Al and Fe (mainly as metal-humus complexes) in the B horizon and a relative enrichment of silica in the A horizon (STEFANOVITS *et al.* 1999). This soil sample is classified as Leptic Acrisol (humic, siltic).

All of the investigations were performed on air-dried and passed through a 2 mm sieve samples. The pH was measured by potentiometric method which was based on Hungarian Standard (MSZ 08-0206-2:1978) while the total carbonate content was measured by gravimetric method (DEAN 1974). The proportion of clay-sized (< 0.002 mm) fraction in the soil samples was determined by an Analysette 22 MicroTec plus laser

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sedigraph (FRITSCH, Idar-Oberstein, Germany). The soil mineral composition was measured on desorientated aggregates from < 0.002 mm fraction using an X-ray diffractometer (XRD) (Rigaku Ultima IV, RIGAKU, Tokyo, Japan). ROM fraction was isolated by the chemical method reported by QUÉENÉA *et al.* 2005.

The RE analyses were performed with a Standard RE-6 pyrolyzer using the “Bulk Rock” method. Samples were heated to 180°C for 3 min, followed by a programmed heating at 25°C/min under nitrogen flow up to 650°C. The residues were combusted in a stream of air up to 850°C (LAFARGUE *et al.* 1998). The mathematical deconvolution of the S2 integral curves was performed by a method which has been reported by HETÉNYI *et al.* (2005) and SEBAG *et al.* (2006). RE pyrolysis has been used by petroleum industry for decades and has become a standard tool for hydrocarbon exploration (LAFARGUE *et al.* 1998). Nowadays several researches have pointed out that this technique could be well suited for characterization of the OM in soils and also recent sediments (DISNAR *et al.* 2003; SEBAG *et al.* 2006; TAMBACH *et al.* 2009). RE analysis is composed of two steps, a pyrolysis in an inert atmosphere (nitrogen) and an oxidation in air. In the pyrolysis stage the free hydrocarbons, present in the sample (S1 peak), at 180°C and hydrocarbon produced by thermal cracking of OM (S2 peak) with increasing temperature from 180°C to 650°C are recorded with a flame ionization detector. Under pyrolysis the amount of CO and CO₂ which released during cracking of OM (S3 curves) is measured by an infrared detector. After pyrolysis the residual organic carbon is determined by oxidation under air with the infrared detector, too. During the oxidation CO₂ and CO was formed from remaining organic carbon which was recorded as S4 curves. The TOC is calculated from the pyrolyzable carbon (PC) released as hydrocarbon compounds, CO, and CO₂ during pyrolysis (S1, S2, and S3), and residual carbon (RC), released as CO and CO₂ in oxidation process (S4). The T_{peak} is the temperature measured at the maximum of S2 peak by a RE6 pyrolyzer (Vinci Technologies, Nanterre, France) when producing the maximum amount of hydrocarbons (S2 curve) during pyrolysis. The classical T_{max} value, determined by previous RE models, is a well-known maturity indicator of OM and it is by 40°C lower than T_{peak} (DISNAR *et al.* 2003). The HI is defined as a ratio of S2/TOC and OI is defined as S3/TOC and these values correlate with atomic H/C and O/C values, respectively (DISNAR *et al.* 2003). The RE6 appa-

ratus can calculate two oxygen indices, which are OI_{CO} and OI_{CO2}, the total O₂ content can be calculated as OI_{RE6}. In addition, the shape of S2 curves depends on organic components of SOM because these components have different thermal stability. The relative contribution of the four major classes of organic constituents with different thermal stability (referred to as F1, F2, F3, and F4) can be estimated by mathematical deconvolution of S2 pyrogram (SEBAG *et al.* 2006; NYILAS *et al.* 2008): F1 are the labile (fresh plant and litter), F2 are resistant (lignin and cellulose) bio-macromolecules while F3 are immature geo-macromolecules (humic substances) and F4 are the mature refractory geo-macromolecules (naturally stable biological compounds, OM stabilized by physico-chemical processes and black carbon). From these fraction other indices can be calculated such as R = F1/F2, which shows the ratio of the relative contribution of labile and resistant biological constituents and I = log [(F1 + F2)/F3] which indicates the degree of OM transformation.

RESULTS AND DISCUSSION

According to the composition of the parent material of the studied soils, the carbonate content is the highest in Leptosol, lower in Luvisol, and Acrisol is a carbonate-free sample. Leptosol has nearly neutral pH, Luvisol is an acidic soil, while Acrisol is a strongly acidic soil (Table 1). The proportion of clay size fraction decreases with pH from Leptosol to Acrisol. The ratios of clay-size fraction are 9.5, 5.5, and 2.3% in Leptosol, Luvisol, and Acrisol, respectively.

Bulk RE data showed a remarkable difference in the amount and a moderate difference in the quality of SOM for Acrisol relative to Leptosol and Luvisol (Table 1). The essentially higher TOC content in Acrisol can be a consequence of the thick litter-layer and of the continuous great supply from the fresh plant material, and some contribution of well-preserved waxes from the conifer needle can also increase the amount of the source biomass. In agreement with the present vegetation, the moderate HI, the great OI indices, and the OI_{CO2}/OI_{CO} ratios display terrigenous plants as precursors of SOM for all the three samples. OI_{CO} indices, ranging between 78 and 116 mg CO/g TOC (Table 2), correspond to fresh terrigenous biota, as was reported by CARRIE *et al.* (2012). The terrigenous origin of SOM is confirmed by OI_{CO} indices measured on pure cellulose and lignin (96 and 131 mg CO/g TOC) (HETÉNYI & NYILAS 2014).

Table 1. Main characteristics, basic soil chemical data, and bulk Rock-Eval (RE) data for depth profiles of the studied soils

Soil group	Bedrock	Parent material	Plant cover	Horizon	Depth (cm)	pH	CaCO ₃ (%)	TOC (%)	HI	OI _{RE6}	HI/OI _{RE6}
Leptosol	limestone	limestone and red clay mixture	beech and oak forest	A	0–10	6.5	4.3	6.66	191	250	0.77
				AC	10–20	5.8	4.8	3.77	141	250	0.56
Luvisol	limestone	calcareous-sandy sediment	hornbeam and oak forest	E	0–15	5.0	1.8	4.95	149	362	0.41
				E/Bt	15–30	4.2	1.8	1.37	186	262	0.71
				E/Bt1	30–45	4.3	2.3	0.59	80	367	0.22
Acrisol	whiteschist	whiteschist	beech-oak dotted with pines	A	0–15	3.8	0.0	18.21	172	328	0.52
				E	15–35	3.9	0.0	2.3	190	371	0.51
				B	35–60	4.0	0.0	0.73	96	560	0.17

TOC – total organic carbon; HI – hydrogen index; OI – oxygen index;

HI/OI_{RE6} ratios, which are considered as reliable indicators for the transformation of SOM (DISNAR *et al.* 2003; HETÉNYI *et al.* 2005), reflect the more advanced transformation of SOM in the A-horizon of Luvisol (0.41) and Acrisol (0.52) than Leptosol (0.77). It is confirmed by the relative proportions of major OM classes to the SOM, calculated from the mathematical deconvolution of RE pyrogram (S2) (Figure 1 and Table 3). Despite the same source material of SOM in all soil samples, Leptosol has a higher proportion of bio-macromolecules (43.6%) than Luvisol (35.6%) and Acrisol (32.1%). In agreement with the higher proportion of bio-macromolecules, the greatest value (–0.04) of the I-index also reflects the relatively good preservation of source OM in the A-horizon of Leptosol. The higher relative contribu-

tions of the more stable, more condensed organic compounds are displayed both by the lower HI/OI_{RE6} and conspicuously more negative I-indices in Luvisol (–0.22) and Acrisol (–0.29). Besides the large difference observed in the degree of preservation, the decreased dominance of the labile compounds relative to more resistant ones suggests that leaching can play an important role in controlling the composition of SOM. If we consider only the pH as the main environmental factor which influences the composition of SOM, the highly soluble compounds, such as fulvic acids, formed as predominant compounds, could have resulted in the highest HI/OI_{RE6} value for Acrisol (pH 3.8). However, the about 1.5 times higher HI/OI_{RE6} determined for Leptosol (pH 6.5) than for Acrisol (pH 3.8), suggests the dominance of

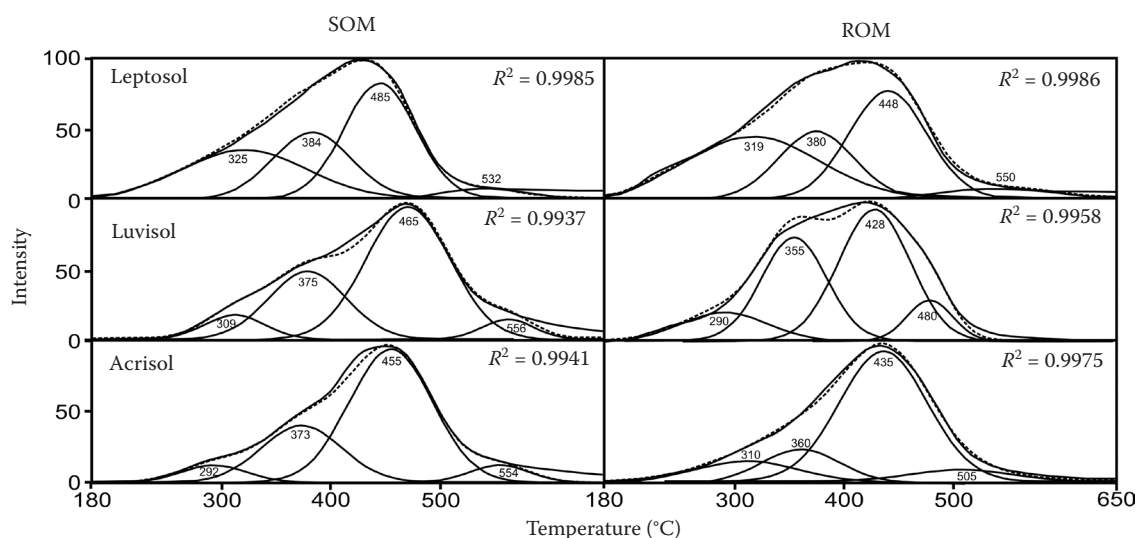


Figure 1. Mathematical deconvolution of Rock-Eval (RE) pyrogram of soil organic matter (SOM) and refractory organic matter (ROM) for A-horizons of the investigated soil samples

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the effect of leaching. From the A-horizons of Acrisol and Luvisol the soluble compounds were leached and so the stable and mature OM could be accumulated. This more transformed OM is very condensed and contains fewer side chains of organic compounds with low HI. Due to the compact clay layer under the A-horizon and the lack of accumulation horizon (B-horizon), leaching is very limited in Leptosol.

The above suggestions are also supported by the depth trends of the RE data (Table 1). TOC content decreases with depth for all soils while the quality parameters display leaching in Luvisol and Acrisol. Downward changes observed in the HI, OI, and HI/OI_{RE6} ratios of three samples correspond to the general evolution trend of SOM. DISNAR *et al.* (2003) demonstrated that the various soil horizons mostly show decreasing HI values with increasing depth in the soil profiles and thus increasing humification. OI values increase from the upper layers down to the B horizon. These data reflect different stages of transformation as a function of depth for the studied samples. The E horizon, which is the lower part of A horizon, has higher HI value than the A horizon indicating the leaching for Acrisol and Luvisol. Additionally, the HI/OI_{RE6} is the highest and the OI_{RE6} is the lowest in the E horizon of Luvisol. The decreasing trend of HI and especially high increase of HI/OI_{RE6} values, observed for Acrisol, are diagnostic of extensive SOM alteration in podzol B horizons. HI/OI_{RE6} value (0.22) calculated for B horizon of Acrisol is similar to the values (scattered between 0.14 and 0.22) reported by DISNAR *et al.* (2003) for B horizons of humic and duric podzols, which developed in temperate zone under boreal influence. The constant OI and the about 25% change in HI and HI/OI_{RE6} between A and AC horizons of Leptosol indicate dehydrogenation of the source biomass and so the early stage transformation of the OM.

A comparison of the RE data determined for SOM and for chemically resistant, mineral-free ROM fraction (Table 2) provided useful information about the processes which could play important roles in the stabilization of the OM in the A horizon of the individual soils. Bulk RE data, in consistence with the degree of OM preservation calculated from the mathematical deconvolution of the S2 peaks, displayed the importance of the organo-mineral associations in the stabilization of SOM for Leptosol and Luvisol. In comparison with SOM, the HI value and the HI/OI_{RE6} ratios are higher, while the OI value is lower for all ROM samples. However, the degree of the change

is different, the smallest for Acrisol and the greatest for Leptosol. Furthermore, the decrease observed for T_{max} during isolation reflects the easier release of the effluents from mineral-free ROM than from SOM during pyrolysis (ZEGOUAGH *et al.* 2004). The changes in these values are due to the decarboxylation of soil organic molecules which led to removing the O-bearing groups, such as carbohydrates and carboxyls. It has to be considered that the organo-mineral complexes can be formed by these O-containing groups. Destruction of the mineral matrix can free these O-containing groups of organic molecules producing CO₂ and reducing the O-content of the OM (ZEGOUAGH *et al.* 2004; TAMBACH *et al.* 2009). The decreased T_{max} value and CO₂/CO ratio and the increased value of PC and H-content during acidic treatment indicate the importance of minerals in the stabilization of SOM. CARRIE *et al.* (2012) have pointed out that the shifting S2 carbon (PC) into RC can be the consequence of the retardation of OM volatilization by the mineral matrix. The great difference in the changes of the PC/TOC ratios during demineralization of the three samples (Table 2) shows that the mineral compositions of soils play an important role in OM stability. This suggestion

Table 2. Bulk Rock-Eval (RE) data determined on the whole soil samples (SOM) and on the refractory organic matter (ROM)

	Leptosol		Luvisol		Acrisol	
	SOM	ROM	SOM	ROM	SOM	ROM
T _{max} (°C)	410	379	423	372	407	389
TOC (%)	6.7	44.9	4.9	51.8	18.2	54.8
PC (%)	1.84	14.09	1.44	22.49	5.34	19.84
RC (%)	4.82	30.82	3.51	29.31	12.87	34.94
PC/TOC (%)	28	31	29	43	29	36
HI (mg CH/g TOC)	191	289	149	414	172	373
OI _{CO2} (mg CO ₂ /g TOC)	282	127	407	159	376	91
OI _{CO} (mg CO/g TOC)	78	54	116	64	96	39
OI _{CO2} /OI _{CO}	3.62	2.35	3.51	2.48	3.92	2.33
OI _{RE6} (mg O ₂ /g TOC)	250	123	362	152	328	88
HI/OI _{RE6}	0.77	2.35	0.41	2.72	0.52	4.24

TOC – total organic carbon; PC – pyrolyzable carbon; RC – residual carbon; HI – hydrogen index; OI – oxygen index

Table 3. Relative contribution of the labile (F1) and resistant (F2) bio-macromolecules, immature (F3) and mature refractory (F4) geo-macromolecules to the soil organic matter (SOM) and refractory organic matter (ROM)

	Leptosol		Luvisol		Acrisol	
	SOM	ROM	SOM	ROM	SOM	ROM
F1 (%)	20.0	35.8	7.7	12.3	6.4	12.1
F2 (%)	23.6	22.5	27.9	32.8	25.7	14.7
F3 (%)	48.1	37.2	59.2	45.9	62.3	66.9
F4 (%)	8.3	4.6	5.3	9.1	5.6	6.3
R	0.85	1.59	0.27	0.38	0.25	0.82
I	-0.04	0.19	-0.22	-0.01	-0.29	-0.40

R = F1/F2, I (degree of OM transformation) = $\log [(F1 + F2)/F3]$

was confirmed by the changes observed in thermal stability between SOM and ROM displayed by mathematical deconvolution of RE pyrograms (Table 3). F1 + F2, together with the I-values calculated from the deconvolution of pyrograms, showed changes of ratio in bio-macromolecules and geo-macromolecules as a result of demineralization. Leptosol and Luvisol displayed a similar increase in I-values (~ 0.2) and in F1 + F2 ($\sim 77\%$) after demineralization. The increased I-values suggest that the SOM was stabilized as organo-mineral association in the A-horizon of Leptosol and Luvisol. However, the great difference observed in the changes of the PC/TOC ratios during demineralization suggests that different minerals could be responsible for the stabilization of OM in

these two samples. Luvisol contains a higher amount of clay minerals than Leptosol. Besides the 10 Å phase (muscovite \pm illite), which is the dominant clay mineral, a small amount of 14 Å phase (smectite \pm vermiculite \pm chlorite) was also detected in Luvisol (Figure 2). Highly reactive surface sites of montmorillonite, the most ubiquitous expandable clay species in soils, play an important role in the stabilization processes of the SOM (TOMBÁČZ *et al.* 2004). Leptosol contains a lower amount of phyllosilicates but the presence of iron oxides and hydroxides (goethite, hematite, and ferrihydrite) (Figure 2), with a high specific surface area and high density of reactive surficial hydroxyl groups, was also determined. The stabilization of OM was probably controlled mostly by these iron compounds, as it was pointed out for numerous soil samples by EUSTERHUES *et al.* (2003) and TOMBÁČZ *et al.* (2004).

The inverse change of the I-value during demineralization reflects that, in contrast with Leptosol and Luvisol, minerals did not play an important role in the stabilization of OM in the A-horizon of Acrisol. This finding is consistent with the podzolic character of this sample. Podzolization resulted in weathering of primary minerals and decomposition of OM. Soluble OM, as well as Al- and Fe-oxides were intensively leached from the A-horizon into the B-horizon, where they accumulated together with clay minerals. This suggestion is confirmed by the lower relative proportion of biomolecules (F1 + F2) and the higher relative proportion of the more stable transformed OM (F3) in ROM than SOM, indicating that the transforma-

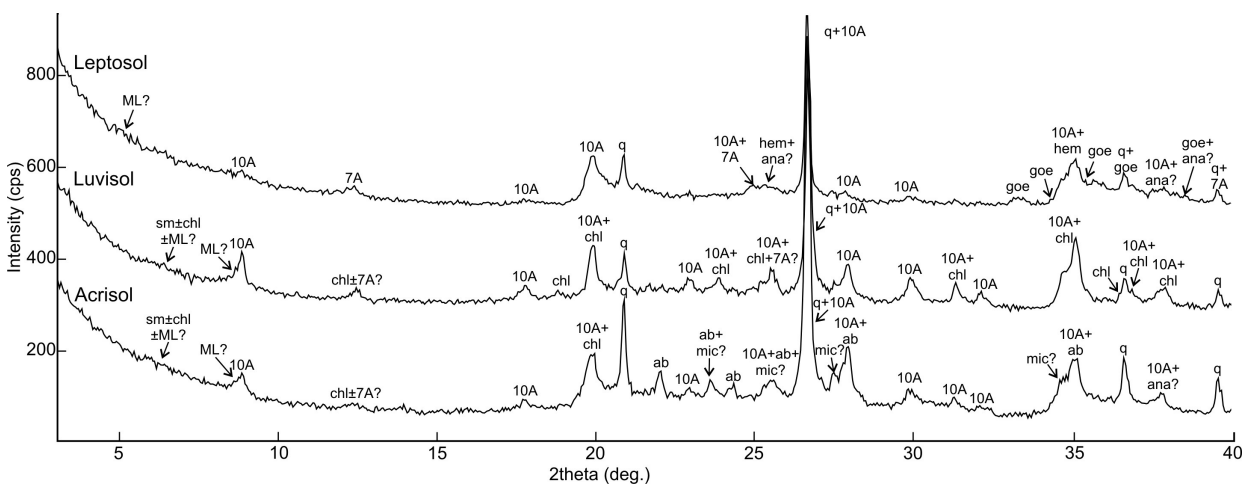


Figure 2. X-ray diffraction (XRD) spectra of the < 0.002 mm grain size fraction for the studied soil samples; q – quartz; 10A – 10 Ångström phase (illite \pm muscovite); ab – albite; ana – anatase; chl – chlorite; ML – mixed-layer phase; 7A – 7 Ångström phase (kandites); mic – microcline; or – ortoclase; phi – phillipsite

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tion of source biomass could be responsible for the stabilization of OM in the A-horizon of Acrisol. The presence of waxes, which are resistant to the acid hydrolysis, could also contribute to the naturally stable OM.

CONCLUSION

The predominance of tree issues, composed mainly of cellulose and lignin, as source material of the SOM in all the three samples formed under the same climatic conditions were shown by the moderate HI and the great OI indices and by the OI_{CO_2}/OI_{CO} ratios.

Despite the same source material of SOM in all soil samples, Leptosol has a higher proportion of bio-macromolecules than Luvisol and Acrisol. The higher proportion of the immature geo-macromolecules (humic substances) and the essentially lower I-index revealed the advanced transformation of the source biomass to the benefit of humic substances in the A-horizon of two forest soils (Luvisol and Acrisol). On the contrary, the good preservation of the plant input in the A-horizon of the lithomorph soil was evidenced by the high relative contribution of the bio-macromolecules, especially of the labile ones.

Our results suggested that the stabilization of the OM in the A horizons of the studied soils was mainly controlled by the parent material of the SOM, pH of the soils, and leaching. In contrast with the two forest soils, where the soluble compounds were leached and so the more stable OM could be accumulated, the more labile components remained in the A-horizon of the lithomorph soil due to the limited leaching.

The comparison of the RE data determined for the SOM and for the mineral-free fraction (ROM) provided useful information about the processes which could play the main roles in the stabilization of the OM in the individual soils. Bulk RE data, in consistence with the degree of OM preservation calculated from the mathematical deconvolution of the S2 peaks, displayed the importance of the organo-mineral associations in the stabilization of SOM for Leptosol and Luvisol. The OM probably associated mainly with iron-oxides and -hydroxides in Leptosol and with clay minerals in Luvisol. In contrast with Leptosol and Luvisol, the stability of the SOM is due to the high relative contribution of the naturally stable biological compounds in Acrisol.

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