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Sustainable forestry and iron compounds in karstic soils: qualitative and semi-quantitative results focused on the occurrence of Fe-compounds on mineral particles

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ABSTRACT: Relic karstic soils in nine localities in the Dinaric Karst in Slovenia, five localities in the Moravian Karst and four localities in the Bohemian Karst were sampled for soil scientific, mineralogical and petrological studies focused on the presentation of descriptive aspects of particular iron compounds. The macroscopy and microscopy of Fe^{2+} and Fe^{3+} compounds were determined and an interpretation of these data was performed aimed at describing sources and their palaeotransports. The presented results show that the studied karstic soils have a heterogeneous petrographical and mineralogical composition when, depending on circumstances, hematite does not dominate and goethite prevails over it or it is an opposite. Results from the chosen methods reinforce sources of the new materials as the crucial factor for the studied karstic soils.

Keywords: iron oxides; iron hydroxides; karstic soils; soil formation in karsts

Sustainable development of inhabited karstic areas is directly linked to the knowledge of particular, karst, phenomena where a keen focus on the conservation of soil ought to be stressed. Preservation of the soil mantle plays a crucial role for the maintenance of the living standard existing in the karst areas. However, the soil cover in karsts is both rather shallow and highly jeopardized by erosion. The value of a forested land in karst is, therefore, closely related to the volume of soil. The presence of thick soil mantles which are not massively jeopardized by erosion grants essential pre-conditions for sustainable forestry.

A great variety of possible sources of materials, and very different possible geochemical microenvironments may result in an extremely variable pattern of soils in relation to the karst surface. The most fertile karstic soils (Red Cambisols/Rubefic Inceptisols) were chosen for agricultural fields and pastures. It appears that the fertile soils originate from the bottoms of palaeocaves. Consequently, the question what such soils have in common, if anything at all, becomes unavoidable. The behaviour of iron compounds is surely one of the characteristics of the *terra rossa,* which have been formed in the karstic environment. This issue is the subject of the paper as a logical development following the work by Šušteršič et al. (2009).

Generally, the karstic soils have typical colours pink, pale red, light red, red, dusky red or dark red, and combinations of red and brown. The comprehensive review of opinions on *terra rossa* definitions was given by Schaetzl and Anderson (2005). The main questions are (i) what the origin of *terra rossa* is (Delgado et al. 2003; Mee et al. 2004), (ii) what various types of *terrae rossa* have in common (Plaster, Sherwood 1971; Khadkikar, Basavaiah 2004), and (iii) what the essence of apparent uniformity is like (Boero, Schwertmann 1989; Miko et al. 1999). Iron oxides play a crucial role in this. Iron oxides are formed when there is an oxygen-rich atmosphere – no red beds older than about 2000 Ma are known (Retallack 2001). In general, the occurrence of red soils is associated with breaks in the sediment accumulation of many thousands of years (Retallack 1994). Red soils can also be formed secondarily as a result of burial processes when reddening occurred in ferric hydroxide minerals in primarily gleyed horizons (McCarthy et al. 1998). Such processes will lead to the extremely high spatial heterogeneity of karstic soils (Mirabella et al. 1992; Ložek 1999) showing very different shares of karstic and non-karstic particles, different waterlogging capacities and a mosaic of slightly acid and neutral soils. Nevertheless, both allochthonous and autochthonous sources have been considered to be of similar importance (Bellanca et al. 1996; Delgado et al. 2003). Merino (2006) and Merino and Banerjee (2008) demonstrated that the loamy material on karst can derive straight from the maternal rock by gradual assimilation. Therefore, the search for the provenance of relic karstic soil materials has to include consideration of overlying sedimentary strata of carbonaceous rocks (Torrent, Cabedo 1986), insoluble residues in limestones (McFadden, Hendricks 1985) and an authigenic clay from the metasomatic zones (Merino 2006).

The names *terrae calcis*/*terra rossa* can be seen as names used for the very ultimate climate conditioned (hematite vs. goethite) products of weathering of completely different materials: there are red/reddish soils in karst, but the formations of the particular ones are very questionable. Presently, the Tertiary and Quaternary sediments and soils have been weathering jointly – the ultimate product is the same but the primary material can be entirely different. A very similar situation occurred throughout geological history, when drier Pre-Pleistocene periods led to red colours. "Karst" is by no means a synonym for "limestone terrain". It is very probable that the evident locational connection between *terra rossa* and limestone terrains is not on the level of rock-to-rock relation but on the level of geo-bio-physical-chemical environment provided by the functioning of the karst geomorphic system.

Moreover, *terra rossa* very likely originates within the karst geomorphic system but does not derive from the karstic rock(s) – the latter might just occasionally provide some mineral components. The interpretation that the term "karst" relates to the "karstic landscape" seems most obvious but it does not make sense logically: if deposits matching the general perception of *terra rossa* (no matter how it is defined) appeared there, it might be attributed to the underlying karstic rocks and not to the karst system. Characteristic loamy bodies cannot be attributed to the supposed characteristic landscape because the karst is just one of many geomorphic systems: like the others, it does not generate mass but it does support mass transfer. It is obvious that the final product of both weathering and humification in karstic areas (Danin et al. 1983; Wen et al. 2001) looks very similar from place to place, but the existent hypotheses about the formation of karstic soils are very divergent. Different processes of removal of weathering products by solifluction and fluvial processes (Durn et al. 1999) result in the very complex character of karst soils. In addition, the role of climatic features is very important (Rejšek 2004): it is evident that drought affects both dissemination of plants and transformation of iron compounds (Stephens 1965; Boero et al. 1992; Leone 2000). Such a fact leads to the occurrence of soil material containing Fe^{3+} or Fe^{2+} compounds. These compounds are chemically attracted particularly to alumosilicates but, dependent on weathering processes, also to oxides, hydroxides and oxyhydroxides. An array of Fe-oxides in various crystalline forms: ferrihydrite, $Fe_3(OH)_8$, $Fe(OH)_3$, lepidocrocite, goethite, hematite or magnetite, may coexist in many soils because of kinetic and weathering changes, constraints on mineral transformations and open system fluctuations in geochemical conditions (Thomson at al. 2006). What is more, the soil material containing Fe^{2+} compounds is often stabilised (Perethyazhko, Sposito 2005) by the presence of inorganic phosphates, organophosphates and biogenic gases (CO_2, H_2 and CH_4).

The extraordinary complexity of development of relic karstic soils is demonstrated by the distinctive hydrology of karsts (Mahler et al. 2004), unique space heterogeneity of karsts (Mirabella et al. 1992; Ložek 2000), and taxonomic sorting where the micromorphological features play the key role for the proper systematic classification. On the level of Great groups, Soil Taxonomy (Soil Survey Staff 2006) classifies them as (i) Rendolls, Argixerolls or Haploxerolls (the Mollisol order), (ii) Haploxeralfs or Rhodoxeralfs (the Alfisol order), and (iii) Xerochrepts (the Inceptisol order). World Reference Base for Soil Resources (IUSS Working Group WRB 2006) designates them as Haplic/Luvic Phaeozems or Chromic Luvisol, or some of the main soil units from the reference soil group of Cambisols.

Studies aimed at understanding roles of surface karstification and semi-autochthonous karst soil material are rare. Based on the level of processes, i.e. total dissolution, the uniformity of final products of both weathering and humification in recent karst areas is likely to be connected with very old pedological and geological processes: a similarity can be seen in intensively weathered soils Nitisols and Ferralsols (IUSS Working Group WRB 2006) or Oxisols (Soil Survey Staff 2006) in recent tropical and subtropical areas which originate from different parent materials but look very similar (Wilding et al. 1983). Considering all of this and emphasizing the essential role of distinctive karstic hydrology (Ford, Williams 1989) and an uncertainty in the verified presence of local alkaline conditions, the authors are aware that no generally valid description of possible alteration/pedogenetic processes can be submitted. Surely, other suggestions can also be taken into consideration, such as Rendolls in Soil Taxonomy (Soil Survey Staff 2006) but the above-mentioned units are tightly related to non-recent karstic soil development on a European scale.

Thus, the main aim of the paper can be seen in the discussion about descriptive aspects of iron compounds of the material presented by Šušteršič et al. (2009). The study proposed will continue the study on 18 selected plots in the Classical Karst in Slovenia, and Bohemian Karst and Moravian Karst in the Czech Republic pointing new aspects related to the conservation of soil cover. The application of the mineralogical and soil scientifically techniques will shed more light on understanding the role of surface karstic features for the conservation of a soil. The investigation has been focused not only on scientific issues but also on an improvement in the knowledge of practical aspects of the importance of surface karst features for sustainable forestry.

Fig. 1. The layout of the study plots is the Dinaric Karst.

Study area

Two approximately west-east traverses were planned across Slovenia and the Czech Republic. The former traverse runs across the Dinaric Karst (Fig. 1) of southern Slovenia: the nine sample locations were approximately uniformly spaced and chosen to cover the most important rocks of the Mesozoic carbonate sequence (continuous, from late Triassic to Palaeocene, and totalling about 7 km in thickness (Šušteršič 2002). In the case of the Bohemian and Moravian Karsts (Fig. 2), which are not continuous, samples were taken from locations previously known to be characterized by *terra rossa*.

(i) Dinaric Karst

Čepovan – location 13°48'E, 46°3'N, elevation 660 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 2,400 mm and overall denudation rate in the area is estimated 60–90 m·Ma^{-1}. Maternal rocks in the wider area belong to the *Dinaric* carbonate sequence. The colour 5YR 5/7 shows a near degree of rubifica-

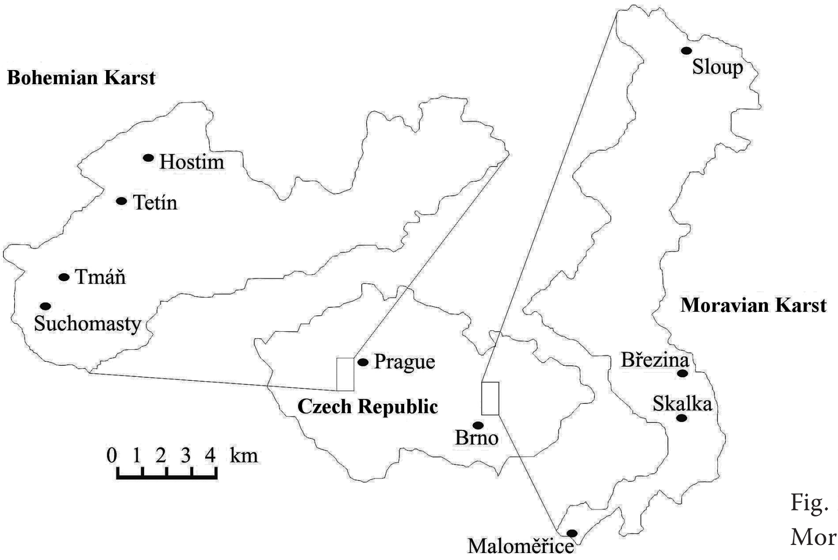

Fig. 2. The layout of the study plots in the Moravian Karst and in the Bohemian Karst

tion. General type of sampled occurrence has been matched as lenses though it is evident that most of the material is of colluvial origin.

Komen – location 13°45'E, 45°49'N, elevation 270 m a.s.l., mean annual temperature 10°C, mean annual precipitation somewhat less than 1,500 mm and overall denudation rate in the area is estimated 20–30 m·Ma^{-1}. Maternal rocks in the wider area are upper Cretaceous, generally pure but locally interbedded by chert, intensively karstified, limestone. The very intense red colour (10R 4/6) indicates a high amount of Fe^{3+} compounds.

Divača – location 13°59'E, 45°40'N, elevation 450 m a.s.l., mean annual temperature a little more than 10°C, mean annual precipitation approximately 1,400 mm and overall denudation rate in the area is estimated 20–30 m·Ma^{-1}. Maternal rocks in the wider area are upper Cretaceous, extremely pure (even > 99.99% $CaCO_3$), intensively karstified, limestone. The prominent red colour (10R 4.5/6) points to very intense rubification.

Laze – location 14°16'E, 45°51'N, elevation 470 m a.s.l., mean annual temperature 8°C, mean annual precipitation over 1,800 mm and overall denudation rate in the area is estimated 60–65 m·Ma^{-1}. At the sampling location the material is clayey and red showing the colour of 10R 5/6 where a high content of Fe^{3+} can be expected.

Verd – location 14°19'E, 45°57'N and 410 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 1,600 mm and overall denudation rate in the area is estimated 60–65 m·Ma^{-1}. The sampled material is red fine loam of 10R 5/6 colour, very intense rubification.

Višnja Gora-Brezje – location 14°46'E, 45°57'N, elevation 380 m a.s.l., mean annual temperature more than 8°C, mean annual precipitation exceeds 1,300 mm and overall denudation rate in the area is estimated 20–40 m·Ma^{-1}. The sample site is approximately 10 m above the toe of a slope in T_3^{2+3} dolomite, mantled by an approximately 10 cm thick layer of reddish brown (2.5YR 4/4) silty material, where a high percentage of Fe-oxyhydroxides can be expected.

Tribuče – location 15°15'E, 45°33'N, elevation 190 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 1,250 mm and overall denudation rate in the area is estimated 65 m·Ma^{-1}. At the spot, it is light red (5YR 6/8) deep soils, where no intense rubification could be expected.

Kočevska Reka – location 14°49'E, 45°34'N, elevation 570 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 1,600 mm and overall denudation rate in the area is estimated 60–100 m·Ma^{-1}. The study plot lies in the Dinaric karst of south-central Slovenia, in the north-westernmost extension of the Moravski ravnik (= Morava flatland).

Lož – location 14°29'E, 45°44'N, elevation 660 m a.s.l., mean annual temperature 6°C, mean annual precipitation approximately 1,500 mm and overall denudation rate in the area is estimated 65 m·Ma^{-1}. The sampled material is clayey and reddish brown (5YR 4/4) and gives an impression to be autochthonous.

(ii) Moravian Karst

Skalka – location 16°45'E, 49°17'N, elevation 460 m a.s.l., mean annual temperature 7.5°C, mean annual precipitation approximately 630 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The pale grey, chemically pure limestone of Vilémovice type is of Devonian-Frasnian age. General type of the sampled occurrence has been matched as pocket. The loamy red material of 10R 4/6 was symptomatic of Fe-oxides high content.

Březina I – location 16°48'E, 49°17'N, elevation 420 m a.s.l., mean annual temperature is 7.5°C, mean annual precipitations approximately 630 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The pale gray, chemically pure limestone of Vilémovice type is of Devonian-Frasnian age. General type of sampled occurrence has been matched as slope material, more generally as lenses. Clay-loamy reddish-brown soil (2.5 YR 4/3) was sampled.

Březina II – location 16°45'E, 49°17'N, elevation 420 m a.s.l., mean annual temperature 7.5°C, mean annual precipitation approximately 630 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The pale grey, chemically pure limestone of Vilémovice type is of Devonian-Frasnian age. General type of sampled occurrence has been matched as unroofed cave, more generally as lenses. The material of very similar colour to Březina I but less clayey and sandier was sampled.

Sloup – location 16°44'E, 49°25'N, elevation 490 m a.s.l., mean annual temperature 6.5°C, mean annual precipitation approximately 680 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study plot on limestone of Vilémovice type Limestone of Macocha strata type is located. The light micrite/dismicrite, chemically pure limestone is of reef edge, splintery fracture type facial characterisation. The grey whitish, partly pinky limestones are of Devonian, Givetian-Frasnian age. The loamy material with a high percentage of sandy particles was prominently red with colour of 10R 4/6. General type of sampled occurrence has been matched as pocket.

Malomeřice – location 16°42'E, 49°13'N, elevation 380 m a.s.l., mean annual temperature 7°C, mean annual precipitation approximately 570 mm with the total summer precipitation less than 350 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study plot is situated on the edge of a limestone quarry “Lesní Lom Brno”, about 2 km north of the Town of Brno. The chemically pure limestone as parent material is of Hády-Říčka type characterised by the dark grey. The limestone comes from Devonian, Upper Famennian age. Loamy material of reddish brown colour (2.5YR 4/4) was sampled. The morphology of the terrain shows an eluvial character. General type of sampled occurrence has been matched as lenses.

(iii) Bohemian Karst

Hostim – location 14°90'E, 49°57'N, elevation 320 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 450 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study plot is a forested karst area developed on clayey limestones of the lower Devonian development of the Bohemian Karst. In the region, Silurian basalts (diabase) and their tuffs are the oldest non-karstic rocks found. Grey fine-grained clayey limestones from Lower Devonian show negligible crystals of secondary calcite due to strong recrystallization. Loamy non-sandy material was light red (10R 6/8). General type of the sampled occurrence has been matched as slope material to lenses.

Tmáň – location 14°40'E, 49°54'N, elevation 390 m a.s.l., mean annual temperature 8.5°C, mean annual precipitation approximately 450 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study area is composed of the whitish and reddish crinoid limestone of Koněprusy-Slivenec type, chemically pure limestones of Devonian, Pragian age. From Upper Palaeozoic, carboniferous conglomerates are the oldest non-karstic rocks, red beds from Stefan include mudstones, siltstones and arkoses. The reddish brown (5YR 4/3) very loamy material was sampled. General type of the sampled occurrence has been matched as in-filled cave, more generally as lenses.

Suchomasty – location 14°50'E, 49°50'N, elevation 340 m a.s.l., mean annual temperature 8.5°C, mean annual precipitation approximately 450 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study plot was developed on the grey and red limestone of Suchomasty type of the Devonian, Lower Eifelian age. The brownish (10R 5/4) parent material was found in the shape of a pocket having calcite cemented clods. The study area is located in a flatland beneath a hilly spot; therefore a share of $CaCO_3$ concretions proving the presence of loess was not surprising. The sampled material was sandy, of loamy character and of reddish brown (2.5YR 5/4) showing a low intensity of rubification. General type of the sampled occurrence has been matched as pocket.

Tetín – location 14°60'E, 49°57'N, elevation 660 m a.s.l., mean annual temperature 8°C, mean annual precipitation approximately 470 mm and overall denudation rate in the area is estimated 20–25 m·Ma^{-1}. The study area is in the dry and warm part of Bohemian Karst. The limestone is of Řeporyje-Loděnice type, grey and varied spotted limestone, Devonian, Pragian. The general character of sampling site appears to be described as partly heavily weathered eluvium, partly sediments which were modified by fluvial transport. Sandy, loamy material implies intense rubification (105 4.5/6). General type of the sampled occurrence has been matched as complex lenses, possibly alluvium/lenses.

METHODS

At all locations, the general characteristics of the occurrence were determined and samples of soil in C horizon were taken for further pedological and geological analyses. Based on design-based sampling, three independent sampling plots for each of the soils were randomly chosen. From each sampling plot, three individual soil samples of the purely mineral horizon were extracted and mixed together. Subsequently, the composite samples were analysed in three replicates.

The colour was determined by Munsell Soil Colour Company (2000). All laboratory analyses of loamy material were done in three replicates. Particle-size classes were determined in the U.S.D.A. system (diameters of 0.002–0.05–0.1–2 mm) by the pipette method (Kalra, Maynard 1991). Soil reaction was measured in an air-dried soil-water suspension (1:5 v/v, shaken for 5 min) at room temperature either in demineralised water or 0.05 mol·l^{-1} $CaCl_2$ (ISO/DIS 10390, 1992). Calcium carbonate content was determined volumetrically (ISO/DIS 10693, 1993). Sorption parameters were determined by $BaCl_2$ (Mehlich 1978).

The bulk clay mineralogy of the samples was determined by the Geological Survey of Slovenia using X-ray diffraction techniques. The clay fraction < 2 µm was separated by centrifuging. The clays were analysed after vapour solvation with ethylene glycol for 12 h at 65°C. Samples were scanned using a Philips PW 3710

X-ray diffractometer with a 1,820 goniometer, an automatic divergence slit, and a curved-crystal graphite monochromator. The instrument was operated at 40 kV and 30 mA using CuK α radiation. Bulk samples of clay fractions were scanned from 2 to 70° 2Θ with step scan 0.02 and step time 1 s. The bulk mineralogy was determined on whole powder mounts.

Semi-quantitative mineralogical compositions of the bulk soil samples and clay fraction were calculated using the methods of SCHULTZ (1964) and MISIC (1999). The calculations are given in wt (%) on the basis of the amount of clay fraction in the soils. The interstratified clay minerals of I/M (illite/montmorillonite) type were determined according to MOORE and REYNOLDS (1997).

The macroscopy of iron oxides was analysed by the rubbing to powder method according to Isakov (ROSICKÝ, KONTA 1961) and chemical determinations of Fe^{2+} by $K_3Fe(CN)_6$ and of Fe^{3+} by $K_4Fe(CN)_6{\cdot}4H_2O$ (WARNE 1962) were applied, i.e. the screening methods of Fe^{2+}/Fe^{3+}-containing compounds/minerals identifications were carried out by the very intensive acid disintegration of sample by the Isakov powder method (ROSICKÝ, KONTA 1961). The Fe^{2+} and Fe^{3+} compounds were distinguished by a staining technique, when weakly (pH ~ 5.0), medium (pH ~ 2.0) and strongly (pH ~ 1.0) acid solutions of HCl with additions of $K_3Fe(CN)_6$ for Fe^{2+}, and $K_4Fe(CN)_6{\cdot}4H_2O$ for Fe^{3+} exhibition (WARNE 1962; DEER et al. 1992) were applied. For the magnetite identification, a simple assay by a strong permanent magnet was carried out.

The microscope techniques (BLOSS 1999) included microscoping of soil in its original state, under dispersion in immersion liquids and in determining solutions based on the optical morphological taxonomy of iron crystals, aggregates and mineral particles by YARDLEY et al. (1990) and DELVIGNE (1998). Four methods were used: (i) chemical determinations of Fe^{2+} by $K_3Fe(CN)_6$ and of Fe^{3+} by $K_4Fe(CN)_6{\cdot}4H_2O$ (WARNE 1962), (ii) chemical determination of iron compounds according to MEITES (1963), (iii) chemical identification of bonds between iron compounds and carbonates according to ADAMS et al. (1984), and (iv) simple assay by a strong permanent magnet.

RESULTS

Soil properties

As for the textural classes of soil samples, the textural class "loamy" was found out in the majority of samples. Besides, we sampled four clay-loamy horizons – two in the Dinaric Karst in Slovenia, Divača (Sample No. 6) and Lož (Sample No. 18), and both sampled horizons in Březina I (Samples No. 21 and 22) in the Moravian Karst. In the Bohemian Karst, on the contrary, Suchomasty (Samples No. 31 and 32) and Tetín (Samples No. 33 and 34) showed only sandy textural classes. In addition, in three horizons in the Dynaric Karst in Slovenia the combination of high percentage of fine sand and low percentage of clay was found – Čepovan (Sample No. 1), Komen (Sample No. 4) and Tribuče (Sample No. 14), where the sandy material came from fragments of sandstones mixed into the fine matrix. In general, the soils in the Moravian Karst display higher similarity in the character of textural classes to the soils in the Dinaric Karst in Slovenia than to the soils in the Bohemian Karst.

Except for Maloměřice, the highest pH values are found in soils in the Moravian Karst where the soils are slightly alkaline (SPARKS 1995). Soils in the Bohemian Karst are neutral and slightly alkaline. Soils in the Dinaric Karst vary considerably – from extremely acid in Komen, mixed with a chert, to neutral in Višnja Gora-Breze. There is a very good relation between carbonate content and soil reaction, including data in Table 1. Soils in the Dinaric Karst in Slovenia contain hardly any carbonates, which can be related to generally more humid conditions. Among all localities in the Czech Republic, only in Maloměřice did carbonates not occur in the studied soil – but the soil material in Maloměřice study plot contained chert particles. Soils in the Moravian Karst showed the highest cation exchange capacity (CEC), which is associated with the other chemical properties. Dealing with relations to physical properties, there is an evident linkage between clay content and CEC seen in the Bohemian Karst, where sandy loamy soils demonstrate much lower CEC than loamy soils. In the Dinaric Karst of Slovenia, the data presented showed no clear interrelationships between the physical and chemical properties. The data also showed no clear interrelationships within chemical properties above.

Macroscopy of iron compounds

Table 2 shows the grouping of soils studied into three main groups according to colour, and related to iron content. When iron content evaluations are performed, the most important data come from a division of iron compounds into iron in its reduced form Fe^{2+} and in its oxidized form Fe^{3+}. The red-

Table 1. Physical and chemical properties of the soils studied.

Area	Study plot	Sample No.	Depth (cm)	Soil colour (Munsell C.C. 2000)	Textural classes (% w)[1]				pH[2]/H$_2$0	pH/CaCl$_2$	CaCO$_3$ (%)[3]	CEC	TEB	BS (%)[4]
					clay	silt	fine sand	sand				(mmol·100 g^{-1})		
Dinaric karst of southern Slovenia	Čepovan	1	32–35	2.5YR 5/8	28.7	39.6	24.6	7.1	4.88	4.67	0.00	25,30	3,00	11,86
		2	35→	10YR 6/6	31.0	36.0	23.4	9.6	5.50	5.39	0.00	16,70	2,00	11,98
	Komen	3	32–45	2.5YR 3/8	37.0	23.1	23.1	16.8	3.92	3.66	0.00	35,40	6,90	19,49
		4	45→	10R5.5/8	29.5	31.0	25.3	14.2	3.79	3.48	0.00	30,30	3,10	10,23
	Divača	5	16–35	10R 3/6	44.0	34.4	17.6	4.0	6.60	6.38	0.10	33,50	25,00	74,63
		6	35→	10R 3.5/6	48.9	34.0	15.0	2.1	5.66	5.41	0.00	31,60	19,70	62,34
	Laze	7	8–18	10R 3.5/6	35.6	30.4	26.1	7.9	4.97	4.73	0.10	38,90	20,90	53,73
		8	18→	2.5YR 5/8	41.3	30.8	24.0	3.9	4.92	4.77	0.00	43,00	26,20	60,93
	Verd	9	15–40	2.5YR 4/8	31.7	26.3	26.9	15.1	4.96	4.82	0.00	38,30	22,20	57,96
		10	40→	2.5YR 4/8	34.1	27.1	22.4	16.4	5.82	5.71	0.10	35,40	29,50	83,33
	Višnja Gora – Breze	11	45–110	2.5 YR 4.5/6	35.1	33.9	27.2	3.8	7.14	6.91	0.20	22,70	22,70	100,00
		12	110→	10YR 4/6	41.1	23.1	25.1	10.7	7.09	6.93	0.10	30,00	28,60	95,33
	Tribuče	13	18–55	2.5R 4.5/8	30.5	32.4	24.6	12.5	4.39	4.07	0.00	17,40	7,10	40,80
		14	55→	5YR 6/8	25.5	34.1	27.4	13.0	4.34	3.87	0.02	18,40	7,70	41,85
	Kočevska Reka	15	28–55	2.5R 5.5/8	31.7	27.8	30.5	10.0	4.39	4.12	0.00	27,90	9,90	35,48
		16	55→	7.5YR 6/7	36.1	30.1	28.9	4.9	4.33	4.05	0.00	27,90	10,50	37,63
	Lož	17	20–60	5YR 4.5/8	44.2	39.0	13.3	3.5	6.95	6.74	0.30	30,70	19,30	62,87
		18	60→	5YR 5/8	58.6	32.0	8.4	1.0	6.76	6.61	0.10	27,50	24,20	88,00
Moravan Karst	Skalka	19	42–60	10^{1}R 4/8	31.9	21.6	22.4	24.1	7.37	7.17	23.20	42,30	ND	ND
		20	60→	10R 4/6	33.6	20.8	17.6	28.0	7.47	7.26	33.60	39,20	ND	ND
	Březina I	21	48–65	2.ZYR 4.5/6	45.5	24.0	16.1	14.4	7.33	7.19	12.80	46,80	ND	ND
		22	65→	10YR 5/7	46.5	20.6	16.5	16.4	7.41	7.20	11.20	46,80	ND	ND
	Březina II	23	29–45	2.5YR 5/4	41.3	25.4	17.1	16.2	7.50	7.31	10.20	45,50	ND	ND
		24	45→	10YR 4/6	30.8	21.7	11.3	36.2	7.55	7.34	31.20	31,80	ND	ND
	Sloup	25	20-45	2.5YR 4/8	35.2	20.6	16.4	27.8	7.57	7.34	17.60	26,20	ND	ND
		26	45→	10R 4/6	39.9	21.8	12.3	26.0	7.36	7.26	18.40	24,00	ND	ND
	Maloměřice	35	32–55	2.5YR 5/6	31.1	42.6	14.0	12.3	6.00	5.79	0.00	29,10	26,60	91,41
		36	55→	7.5R 4/6	44.0	41.0	7.8	7.2	5.83	5.46	0.00	37,70	35,70	94,69

Bohemian Karst	Hostim	27	28–45	7.5R 5.5/8	35.4	29.9	15.3	19.4	7.12	7.01	0.80	36,60	ND	ND
		28	45→	10R 6/8	42.3	30.8	16.9	10.0	7.26	7.12	7.20	32,50	ND	ND
	Tmáň	29	12–35	5YR 4.5/8	39.7	34.3	13.0	13.0	6.90	6.64	2.80	35,80	ND	ND
		30	35→	10YR 4/6	35.9	34.2	13.5	16.4	7.12	6.83	2.40	37,50	ND	ND
	Suchomasty	31	21–60	2.5 YR 6/8	28.2	25.1	14.8	31.9	7.71	7.39	24.80	21,20	ND	ND
		32	60→	10YR 5/8	21.8	22.4	20.3	35.5	7.70	7.39	9.00	22,40	ND	ND
	Tetín	33	26–55	10R 3.5/6	29.3	25.7	18.4	26.6	7.56	7.32	1.30	24,10	ND	ND
		34	55→	2.5R 4.5/6	23.1	27.8	19.4	29.7	7.57	7.27	0.40	19,60	ND	ND

[1]particle-size classes were determined in U.S.D.A. system (diameters of 0.002–0.05–0.1–2 mm) by the pipette method (Kalra and Maynard, 1991), [2]soil reaction was measured from air-dried soil-water suspension (1:5 v/v, shaken for 5 min; 0.05 mol·l^{-1} $CaCl_2$) at room temperature (ISO/DIS 10390, 1992), [3]calcium carbonate content was determined volumetrically (ISO/DIS 10693, 1993), [4]sorption parameters were determined by $BaCl_2$ (Mehlich 1978). ND – base saturation was not measurable because of $CaCO_3$ content higher than 0.3%. CEC – cation exchange capacity (the cation charge adsorbed), TEB – total exchangeable bases (the sum of the exchangeable basic cation), BS – base saturation (the percentage proportion of the CEC that is occupied by the basic cation)

dish colour of soils is caused by oxidized trivalent iron compounds. It is apparent that in the relic soils studied, oxidized iron compounds clearly dominate over reduced iron forms. Though there is a distribution of red, weak red and reddish brown, all three hues appear uniformly distributed in the three karst areas. The highest rate of oxidized iron was found in soils from the Dinaric Karst in Slovenia. According to Munsell Soil Colour Charts (2000), the typically red colour was determined in both Moravian (Sloup, Skalka) and Bohemian (Tetín) karsts. Prominent reactions on oxidized iron were also detected in soils from both Moravian (Maloměřice) and Bohemian (Tetín, Tmáň) karsts. Fragments of chert were found in soils from Višnja Gora-Breze, Komen and Maloměřice by a microscopic assay.

Mineralogy of clay fraction of soils

Tables 3 and 4 show the grouping of soils on the basis of their mineralogical compositions. They are given in wt (%) and calculated on the basis of the amount of clay fraction shown in Table 1. It can be seen that clay fractions of Slovenian soils contain illite, chlorite quartz, calcite, gibbsite, and goethite. The soils from the Czech Republic contain illite, kaolinite, Ca – montmorillonite, mixed-layered minerals of illite/montmorillonite (with random, Reichweite = 0 interstratifications), quartz, calcite, goethite and hematite. The differences in clay mineral contents of soils between the Slovenian and the Czech Republic locations are presented on the radar chart in Fig. 3.

Microscopy of iron oxides

Table 2 also presents the qualitative and semi-quantitative results focused on occurrence, valence and chemical bonds of iron compounds on soil mineral particles. Based on the results of microscopy study and on the chemical results from the staining of sections (Waychunas 1991; Deer et al. 1992) iron compounds were found in six forms describing forms/bonds of Fe^{3+}:

(i) oxidized iron compounds bound to silty particles (mixtures of hydrated Fe-oxides and hydroxides including very fine particles with dimensions less than 0.001 mm may be seen as pigments),

(ii) microscopic soil concretions with goethite (mixture of goethite and lepidocrocite),

(iii) microscopic soil concretions with magnetite, showing high magnetic attraction and containing both Fe^{2+} and Fe^{3+},

Table 2. The intensity of red colour and the type/degree of iron compounds present, the occurrence, the valence and the chemical bonds of iron compounds on soil mineral particles. The study plots are grouped by their joint features. Positive scores are marked by A (for the reaction with acid solution due to the intensity of it as AA), negative statement as a blank square, weak reactions as +

Study plot/sample No.	Soil colour (Munsell Color Company 2000)	Colour			Rubbing to powder method[1]		Chemical determination[2]		Magnetic attraction	An occurence of the iron compounds (in % vol)[3]					Concretions cemented by calcite[4]	Reaction with acid solutions	Magnetic attraction
		red-dish brown	weak red	red	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}		Fe^{3+} bound to silt	Fe^{3+} bound goe-thite	Fe^{3+} bound mag-netite	Fe^{3+} bound hema-tite	iron coats on quartz			
Čepovan/2	105YR 6/6	A			A	A		A		80	10	+					
Višnja Gora Breze/12	10YR 4/6	A			+	A		A		40	40		+	10			
Maloměřice/36	7.5R 4/6	A			+			A		40	10			10			
Verd/10	2.5YR 4/8			A	+	A		A	A	40		10	40	+			A
Laze/8	2.5YR 5/8			A	+	A		A		40			40	+			
Komen/4	10R 5.5/8			A	+	A		A	A	30			70	+			A
Divača/6	10R 3.5/6			A	+	A		A	A	30		+	70	+			A
Kočevska Reka/16	7.5YR 6/7		A		+	+		A	A	30	30	5		10			A
Lož/18	5YR 5/8	A			+	+		A	A	30	30	5		10			A
Tribuče/14	5YR 6/8		A		+	+		A	A	10	30	+		10			A
Tetín/34	2.5R 4.5/6			A	+			A	A	10	30	+	5	5	30	AA	A
Březina I /22	10YR 5/7	A			+	+		+		30	10			10	30	AA	
Tmáň/30	10YR 4/6	A			+	+		A		30	10			10	30	AA	
Hostim/28	10R 6/8		A		+	+		+	A	30		5		10	30	AA	A
Suchomasty/32	10YR 5/8	A			+	+		+	A	20	+	5		5	30	AA	A
Sloup/26	10R 4/6			A	+	+		+	A		5	+	30	5	30	AA	A
Březina II/24	10YR 4/6	A			+	+		+					20	+	30	AA	
Skalka/20	10R 4/6			A	+	+		+					20		30	AA	

[1] rubbing to powder method by Isakov (Rosický, Konta 1961), [2] chemical determinations of Fe^{2+} by $K_3Fe(CN)_6$ and of Fe^{3+} by $K_4Fe(CN)_6.4H_2O$ (Warne 1962), [3] chemical determinations of Fe^{2+} by $K_3Fe(CN)_6$ and of Fe^{3+} by $K_4Fe(CN)6.4H_2O$ (Warne 1962) and chemical determination of iron compounds by Meites (1963), [4] chemical identification of bounds between iron compounds and carbonates by Adams et al. (1984)

Table 3. Bulk sample mineral composition of clay fraction from Slovenian, Moravian and Bohemian karstic soils (in % w), calculated on amount of clay fraction

Study plot/sample No.	Ill	Chl	Kln	Mnt	I/M R0	Qtz	Cal	Gbs	Gt	Hem	Clay (%)
Slovenian Karst											
Čepovan/2	10	10	9	0	0	0	0	0	0	0	29
Komen/4	3	15	18	0	0	0	0	0	1	0	37
Divača/6	4	18	18	0	0	0	0	2	1	0	43
Laze/8	5	11	14	0	0	0	0	2	4	0	36
Verd/10	3	11	14	0	0	0	0	2	2	0	32
Višnja Gora-Breze/12	0	15	15	0	0	0	0	2	3	0	35
Tribuče/14	7	8	8	0	0	0	2	3	3	0	31
Kočevska Reka/16	16	5	6	0	0	0	0	3	2	0	32
Lož/18	2	16	18	0	0	0	0	6	3	0	45
Moravian Karst											
Skalka/20	5	0	13	13	0	0	0	0	3	0	34
Březina I/22	3	0	14	26	0	0	0	0	2	0	45
Březina II/24	9	0	15	0	10	0	4	0	3	0	41
Sloup/26	6	0	15	0	6	4	3	0	0	2	36
Maloměřice/36	7	0	12	0	14	7	0	0	3	0	43
Bohemian Karst											
Hostim/28	14	0	4	0	10	5	2	0	0	1	36
Tmáň/30	4	0	10	0	16	6	0	0	3	0	39
Suchomasty/32	2	0	17	0	5	0	0	0	4	0	28
Tetín/34	4	0	16	0	6	0	0	0	4	0	30

Ill – illite; Mnt – montmorillonite; I/M R0 – mixed layered clay mineral illite/montmorillonite with random, R = 0 startification; Chl – chlorite, Kln – kaolinite, Qtz – quartz, Cal – calcite, Gbs – gibsite, Gt – goethite, Hem – hematite

(iv) microscopic soil concretions with hematite (irregularly shaped red concretions where positive reactions on Fe^{3+} appear when concentrated HCl is used),

(v) soil quartz particles of microscopic size coated with Fe^{+},

(vi) microscopic soil concretions cemented by calcite.

Even though a certain amount of products of rubification in Slovenia might be seen as a product of humid Mediterranean conditions, it can be concluded that the colour of soils from the Dinaric Karst of Slovenia is closely related to the geologically presented iron oxides: the microscopic studies showed that the colour of a particle containing iron compounds was mainly affected by the presence of iron compounds in relation to (i) physical bonds (i.e. because of the presence of the very fine-grained, mostly prominently reddish pigments) and (ii) chemical bonds (i.e. because of the pres-

Table 4. Average bulk sample mineral composition of clay fraction from Slovenian, Moravian and Bohemian Karstic soils (in % w) calculated on clay fraction

Study area	Ill	Chl	Kln	Mnt	I/M R0	Qtz	Cal	Gbs	Gt	Hem	Clay (%)
Slovenian	6	12	13	0	0	0	0	2	2	0	35
Moravian	6	0	14	7	6	2	1	0	2	0	38
Bohemian	6	0	12	0	9	3	0	0	3	0	33

Ill – illite, Mnt – montmorillonite, I/M R0 – mixed layered clay mineral illite/montmorillonite with random, R = 0 startification, Chl – chlorite, Kln – kaolinite, Qtz – quartz, Cal – calcite, Gbs – gibsite, Gt – goethite, Hem – hematite

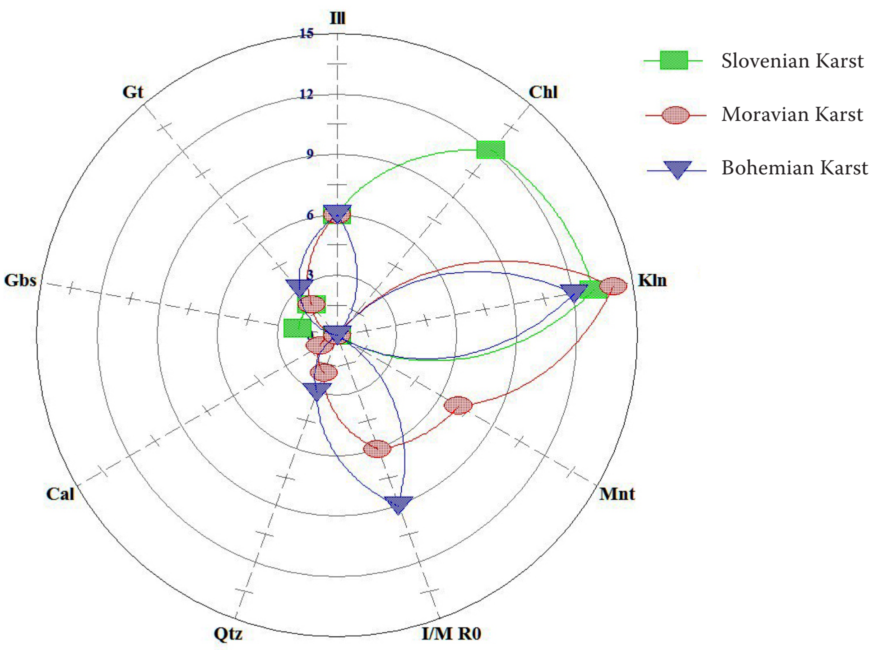

Fig. 3. Average composition of clay fractions from Slovenian, Moravian and Slovenian karstic soils

ence of the chemically bound iron in the form of either Fe^{2+} or Fe^{3+}). As concerns the results documenting the iron behaviour with the karstic setting, the colours of soil particles were derived from the presence of iron compounds bound physically and chemically to other mineral particles such as particles of quartz, carbonates and clay minerals.

DISCUSSION

Which logical category does *terra rossa* fit to, (i) specific mineral aggregate of fixed and stable mineral composition, (ii) approximately uniform mineral aggregate of characteristic colour, (iii) loamy cave sediment of any composition, subsequently exposed at the surface, or (iv) one of the above categories associated with an organic complex, with the mixture displaying a characteristic colour? The colour appears to be a more stable and reliable criterion, though not very exact; various *terra rossa* deposits exhibit quite a wide span of hues (10R-YR). The supposed similarity with lateritization is illusory – laterite contains minerals that derive directly from the parent rock, including Fe hydroxides that are responsible for its characteristic colour. This is not the case of *terra rossa*, where most components are of exotic, non-parent origin. Thus, the basic question must be: what is the fundamental relationship between the karstic geomorphic system and the red colour of *terra rossa* deposits that occur on the karst surface (and are commonly trapped within its fractures)? The first step is to acquire more knowledge of the dynamics of its iron content and particular iron compounds.

The ferrum iron compounds, typical of *terra rossa* (Wright, Wilson 1987; Singer et al. 1998), do not reflect the physicochemical conditions of limestone diagenesis (Delgado et al. 2003). Having in mind that calcite is a congruently dissolving material, it has to be true that it cannot contribute either to soil skeleton or to soil colour. Therefore, karstic soils of any sort must originate from the material somehow alien to calcite, by a process in which the ultimate role of climate (Harden, Taylor 1983) has to be stressed.

The main soil minerals containing iron can be divided into two groups – iron oxides and iron oxyhydroxides (Waychunas 1991; Deer et al. 1992). Hematite α-Fe_2O_3, maghemite γ-Fe_2O_3 and magnetite $Fe^{II}Fe^{III}{}_2O_4$ belong to Fe-oxides, goethite α-FeOOH and lepidocrocite γ-FeOOH to Fe-oxyhydroxides. Hematite and maghemite are mostly red, magnetite is grey; but all of these can also be black. Goethite and lepidocrocite are mostly brown, rarely yellow.

The process of rubification (White 1997) is based on the production of mostly hematite and partly goethite (Sparks 1995) that form coatings on clay and silt particles. The process has recently been observed mostly in subtropical low forests and savannahs, where dry and rainy periods followed one another. In such areas, rubification is commonly seen on well-aerated, base-saturated, slightly acid soils rich in humic acids: neither Moravian not Bohemian Karst has such conditions – the transformations in soil are linked to the production of iron hydroxides from the group of ferrihydrites FeO(OH) and $Fe(OH)_3$, i.e. the process of brunification dominated. The enormously thick red beds come from lake bottoms and alluvial cones that were created mostly in Permian and Palaeogene, when high temperatures throughout the year and heavy rainstorms created conditions for enrichment of products of weathering with oxidized iron compounds (conditions commonly found in fractures in any freshly open quarry front). The data presented support the findings of recent studies on karstic soils (cf. the Introduction), reinforcing the idea that such soils do not turn red due to their pedogenesis but due to the massive presence of staining pigments, i.e. Fe-oxides. The authors are aware that there are no relevant data presented in the paper which give evidence that the colour of recent karstic soils is to be linked to the colour of ancient sediments, but their findings support such an approach. Current local studies (Furlani et al. 2009; Urban, Rzonca 2009) reinforce such conclusions. In spite of that, heterogeneity of relic karstic soils where autochthonous soil particles and allochthonous soil sediments are unambiguously found together makes generalization difficult. The quantitative evaluation in the sequence non-weathered bedrock – transition zone of interchanges within the horizons of soil processes – subsurface soil mineral horizon together with the qualitative evaluation of the role of subsurface lateral water movement from the subsurface reductive conditions, where easily dissolved Fe^{2+} compounds are stable, to the surface oxidative conditions, where not easily dissolved Fe^{3+} are stable, may be an answer to such difficulties.

The data presented can also be related to the production of locally distinctive iron oxides and hydroxides: both favourable aeration and appropriate ingress of air and egress of water, even when there are very clayey soils, play important roles. There is obviously a very important task played by both percolation of rain-water through karstic cracks and favourable structure of the soils themselves: the soil colloids saturated with calcium make a prominent prismatic structure. What is more, eroded materials from non-karstic areas are transported into a karst and eroded autochthonous material is karst transported downwards into caves.

The data obtained, thus, reinforce the role of karstic non-carbonate components. In general, due to the composition of limestone, two different features can be seen: (i) the inner material in cracks is derived from the time when the open space was filled in, and (ii) fragments of limestone are often covered by hematite (tectonic silt). In terms of the insoluble residues, the length and intensity of dissolution and mechanical weathering of limestone play a key role. With respect to the role of palaeocave sediments, one of the strong starting ideas related to the role of palaeokarstic caves in the sense of Bosák et al. (1989) can be reinforced by highlighting the crucial importance of modelling (Kaufmann 2009).

CONCLUSIONS

Inherently negative surface karst features play the most important role for the forestry because of their massive storage of karstic soils. The karstic soils studied were of both the allochthonous and autochthonous origin: (i) karst pockets, protecting the soil very effectively from water and wind erosion, were filled partly by the autochthonous insoluble residues of maternal rock, and (ii) the rest of accumulations of soil and clayey material are evidently of allochthonous origin. Results focused on the occurrence, valence and chemical bonds of iron compounds to soil mineral particles, based on findings of microscopy study and by the chemical staining of sections, iron compounds can be found in the forms of mixtures of hydrated Fe-oxides and hydroxides including very fine particles with dimensions less than 0.001 mm, mixture of goethite and lepidocrocite, microscopic soil concretions with magnetite, microscopic soil concretions with hematite, quartz particles coated with Fe^{+} and concretions cemented by calcite.

Based on the characterisation of iron compounds, the karstic soils studied can be divided into four groups:

(i) karstic soils where concretions with hematite dominate – three localities in the Moravian Karst: Skalka (sample No. 20), Březina II (sample No. 24) and Sloup (sample No. 26),

(ii) karstic soils with joint domination of concretions with hematite and oxidized iron compounds bound to silty particles – four localities in the Dinaric Karst of Slovenia: Komen (sample No. 4), Divača (sample No. 6), Laze (sample No. 8) and Verd (sample No. 10),

(iii) karstic soils with domination of oxidized iron compounds bound to silty particles – two localities in the Moravian Karst and one locality in Slovenia: Čepovan (sample No. 2) in the Dinaric Karst in Slovenia and Březina I (sample No. 22) and Maloměřice (sample No. 36) in the Moravian Karst,

(iv) karstic soils with joint domination of concretions with goethite and oxidized iron compounds bound to silty particles – all localities in the Bohemian Karst and four localities in the Dinaric Karst in Slovenia: Višnja Gora-Brezje (sample No. 12), Tribuče (sample No. 14), Kočevska Reka (sample No. 16) and Lož (sample No. 18) in the Dinaric Karst in Slovenia and Hostim (sample No. 28), Tmáň (sample No. 30), Suchomasty (sample No. 32) and Tetín (sample No. 34) in the Bohemian Karst.

Having in mind the qualitative and semi-quantitative results focused on the occurrence, valence and chemical bonds of iron compounds to soil mineral particles leading towards such aggregation, groups (i) and (iii) do not allow any generalisation. However, the study plots in group (ii) have in common "pure karstification", including a very pure rock as negligible exterior influences. And, general similarity among the study plots in group (iv) is that they are not very distant from non-karstic rock outcrops. The authors are aware that the presented laboratory reports focused on iron compounds in karstic soils, their macroscopy and microscopy are directly linked to samples taken out of the general geo-karstological context. The next step will be focused on relating the results to insoluble residuals from the parent rock in identical study plots (Šušteršič et al. 2009).

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