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Geochemical fingerprint of insoluble material in soil on different limestone formations

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ABSTRACT

In the Karst region near Divača, Slovenia, soils are developed on the limestone of three geological formations: Sežana, Lipica, and Liburnian. In each formation, six soil profiles were dug, limestone insoluble residua was obtained, and in Liburnian Formation interbedded material and material filling fractures and cavities was sampled. All soils have silty clay and silty-clayey loam texture, pH levels in the range 4.5–7.0, high organic matter content and saturation with basic cations over 50%. However, soils on the Sežana Formation are deeper and more evolved, and besides as Rendzic Phaeozem classify also as Eutric Cambisol. Their insoluble residuum is richest in mineral part. The profiles on the Lipica Formation are a Rendzic Phaeozem, and the shallowest soils on the Liburnian Formation are either a Rendzic Phaeozem or a Rendzic Leptosol. Additionally, the soils formed over the Lipica Formation are characterised by a greater portion of the small rock fragments (< 200 g), due to its paleo-karstification. The insoluble residuum of all three formations is rich in organic matter and fine grained. The general soil chemistry is in accordance with highly weathered upper crustal material and, compared to insoluble residua indicates the contribution of material from an additional source. The analysis of variance demonstrated differences in redox-sensitive elements (Cr, Mo, Ni, U, V, and Y) between formations, which are inherited by the insoluble residua. The insoluble residua contributed material and left a specific geochemical fingerprint in the observed soils, but regarding texture and general geochemistry, non-carbonate material must have been added. The material that fills karst forms inside the limestone profile is similar to the soils, but not identical. Other interbedded and probably also eolian material contributed to the final mass.

1. Introduction

The majority of research on soils developed on limestone focused on Mediterranean red soils, which is called *terra rossa* (Yaalon, 1997; Durn et al., 1999; Durn, 2003; Delgado et al., 2003; Merino and Banerjee, 2008; Muhs and Budhan, 2009; Cabadas-Báez et al., 2010; Muhs et al., 2010; Liu et al., 2013; Lucke et al., 2014) as their deep profiles raised a question of in situ formation. Although carbonate rocks prevail in Slovenia (Pleničar et al., 2009), terra rossa covers only 0.2% (Prus and Stepančič, 1995; Vidic et al., 2015). The most common soil types on limestone and dolomite, which overlap 37% of the Slovenian territory, are rendzinas (Leptosols and Phaeozems), brown soils (Cambisols) and leached soils (Luvisols) (Vidic et al., 2015; Vrščaj et al., 2017). Most of the limestone is of the Mesozoic age and is considered pure with a low content of detrital material, i.e., from only 1–2% of insoluble residuum (Gams, 1974, 2003; Ogorelec and Rothe, 1993) to a maximum 9% (Kranjc, 1980; Pleničar and Dozet, 1994). The insoluble residuum content of limestone and dolomite from near Istria, Croatia averages 0.86% (Durn et al., 1999). Even in the case of shallow soils, a large amount of limestone should dissolve to form them. However, some authors (Driese et al., 2003; Šušteršič et al., 2009) have already noted that nonpedogenic strata directly beneath the soil are not necessarily representative of the parent material. In spite of this, we assume that limestones that are sedimented in distinct environments have had various input of compositionally different terrigenous material, which left characteristic geochemical fingerprints in the soils. Moreover, other material besides limestone insoluble residuum, found in the weathering limestone profile, i.e., interbedded material and material filling karst forms, could significantly contribute to the soil profile.

Limestone in the classical Karst region near Divača is of a Cretaceous to Paleocene age and is deposited in several different environments (Jurkovšek et al., 1996, 2013). The 230–500 m thick Upper

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Cretaceous biomicritic Sežana Formation, composed of bedded limestone, locally with chert, formed on a shallow restricted shelf with occasional pulses of littoral, lagoonal, and pelagic influence. It is followed by the 150–400 m thick Lipica Formation, which includes several types of limestone. It was deposited mostly in the opened part of the shelf and locally in its restricted and littoral segment. As in the Sežana Formation sequences of laminated limestone contain chert. Sežana and Lipica Formations are similar in certain lithological and paleoecological characteristics. The Lipica Formation ends with a distinct paleo-karst horizon. After a hiatus, in Paleocene sedimentation begins with a package of freshwater, brackish, and shallow marine carbonates of the Liburnian Formation. Its thickness is from 50 m to over 200 m. Some transitions occur to marly limestones and limestone breccias. Thin layers of coal appear locally (Jurkovšek et al., 1996, 2013).

Prevailing soil types in the Karst region near Divača are rendzinas (40%) and brown soils (50%). Leached soils (10%) only rarely appear (Soil information system/ICPVO, 1999–2015).

The purpose of our research is a pedological, mineralogical and geochemical characterisation of the soils that are developed in the same climatic conditions, in the same topography, and on the generally same limestone bedrock, but on three different limestone formations. We also aim to reveal possible statistically significant differences in their physical and chemical properties. The results would help to enlighten the soil formation on karstic terrains and contribute to the understanding of the role of in situ and ex situ material.

2. Materials and methods

2.1. Research area

The research area is the karst plateau between Lokev and Divača (Fig. 1) in Slovenia. The Sežana (SŽ), Lipica (LIP) and Liburnian (LIBR) Formations are exposed in parallel bends, following each other in a north-south direction. The Sežana Formation is the most northern, and the Liburnian is the most southern (Fig. 1). All limestone beds generally dip to the south, but in the Sežana Formation, at a bit steeper angle (20–30°), than in the Lipica (10°) and Liburnian Formations (10–18°). The Sežana Formation is composed of thick-layered biomicrite limestone that is sedimented in the shallow marine water (Jurkovšek et al., 1996, 2013; Celarc et al., 2012). Within the Sežana Formation, Komen limestone occurs with chert, indicating a lagoonal model of sedimentation with occasional anoxic and dysoxic conditions on the seabed (Jurkovšek et al., 2016). The limestone of the Lipica Formation is mostly thick-bedded to massive with rudist biostromes and bioherms of grainstone to packstone types. Local transitions to biocalcarenite indicate an open shelf environment, and endolithisation shallow shelf. A thin-bedded to laminated variety (wackestone and packstone) is characteristic for an even calmer environment (Jurkovšek et al., 1996, 2013). In some parts, a darker colour, which is caused by organic matter and pyrite, indicates locally reductive conditions. Regional unconformity separates a shallow-marine Cretaceous passive-margin carbonate succession from the limestone of the overlying deposits of the synorogenic Upper Cretaceous/Lower Paleogene Liburnian Formation that is formed at a carbonate platform at the periphery of the foreland basin (Košir and Otoničar, 2001). The unconformity is expressed by an irregular paleokarstic surface that is locally marked by bauxite deposits (Otoničar, 2007). In further progression of the thrusting, the area was submerged and in the freshwater, brackish and marine environment, the darker bituminous limestone of the Liburnian Formation formed. The Paleocene parts of the formation are characterised by darker, local marly limestone (Jurkovšek et al., 2016). At the Cretaceous/Tertiary (K/T) boundary more Ni, V, Sm and Ga (Dolenec et al., 1995; Ogorelec et al., 1995) have been established in the Cretaceous limestones. The synorogenic carbonate platform was finally buried by prograding hemipelagic marls (Otoničar, 2007).

2.2. Sampling

In each of the three formations, we sampled one fresh limestone sample (SŽ-R, LIP-R, and LIBR-R) to obtain insoluble residua (SŽ-InsRe, LIP-InsRe, and LIBR-InsRe). The area has little fresh outcrops. Therefore, sampling of interbedded material and other material present in the limestone profile was restricted. We managed to find only one 4 m deep road-cut in the Liburnian Formation (Fig. 2). We sampled three types of material that was concordant to the limestone beds: one laminated darker rock (Intb 1), a small quantity of muddy material

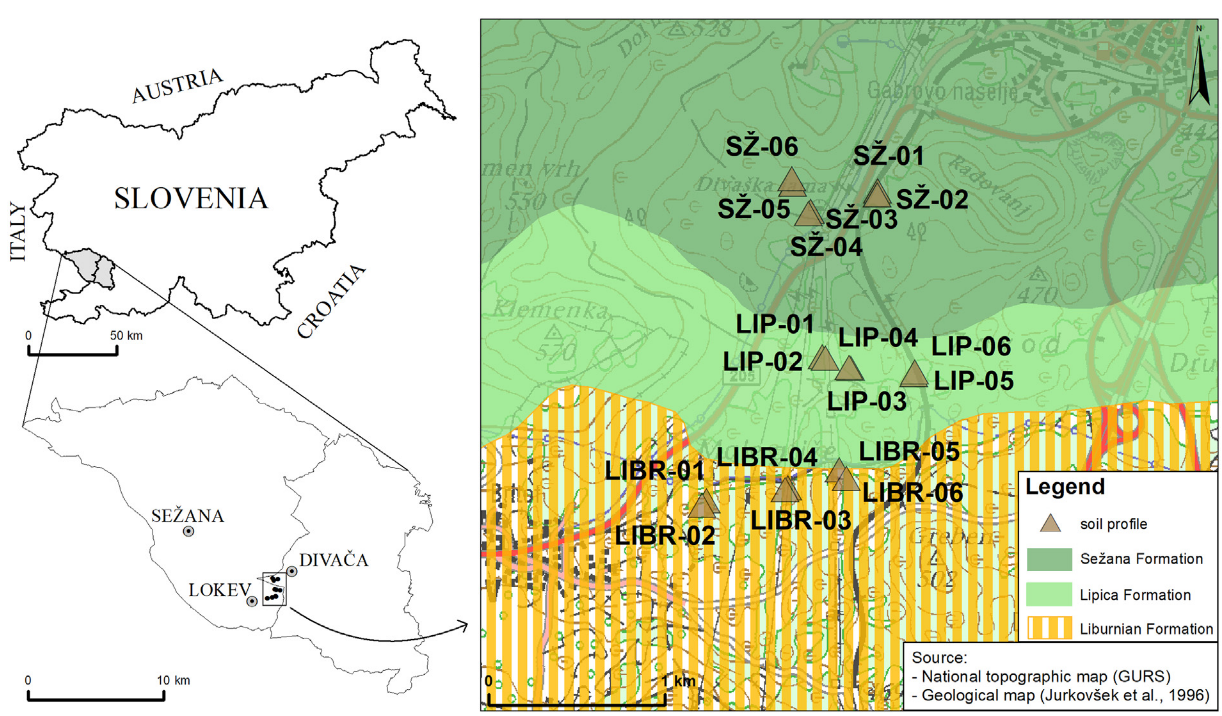

Fig. 1. The position, limestone formations and locations of the soil profiles for the research area.